# Studying competition, disorder and nanoscale fluctuations in strongly correlated systems and the necessity of combining methods such as muons, x-rays and neutrons

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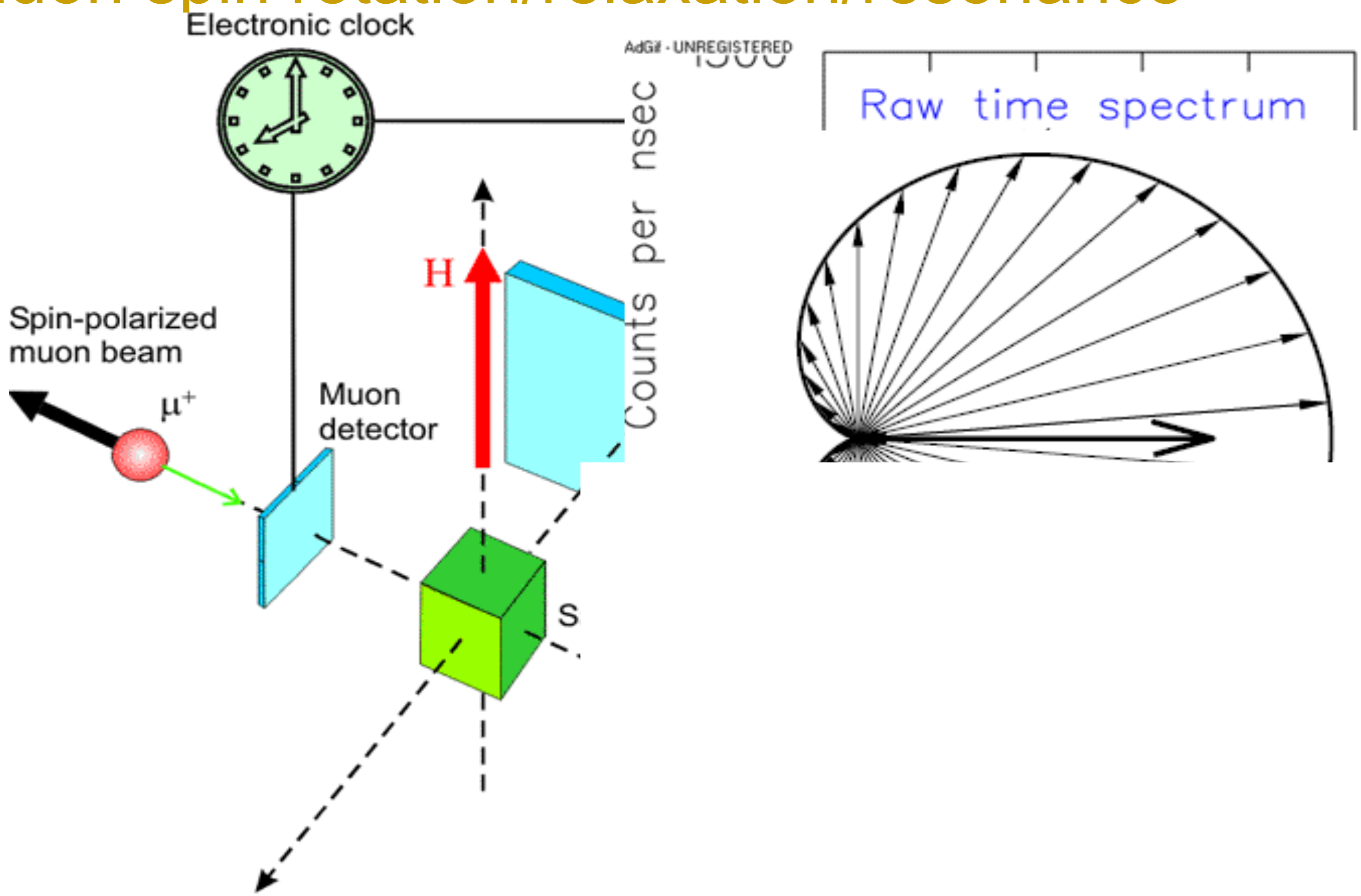
# Why do we love Muons?

- They are a LOCAL probe of the magnetic field in a material:
  - Sensitive to all kinds of spin order (or lack of it): antiferromagnets, spin-gap systems, spin glasses, ferromagnets…
  - follow an order parameter as a function of temperature
  - provides information about internal magnetic field distributions (inhomogeneous fields of phase separation)
  - Provides information about spin dynamics and relaxations
  - it works very well at milli-Kelvin temperatures (the incident muons easily pass through the dilution refrigerator windows)

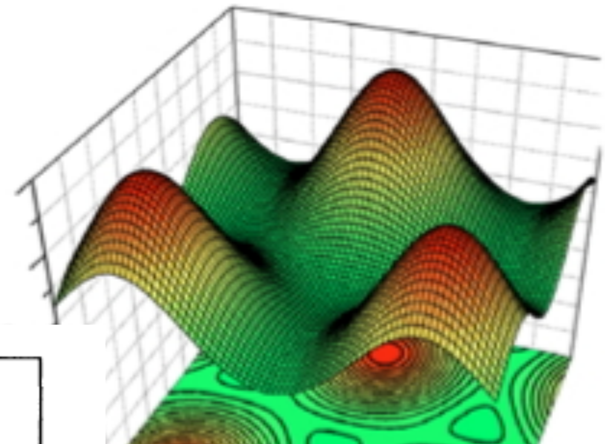
A very versatile probe of magnetism in complex materials

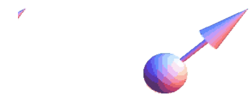
# MuSR: Muon spin rotation/relaxation/resonance

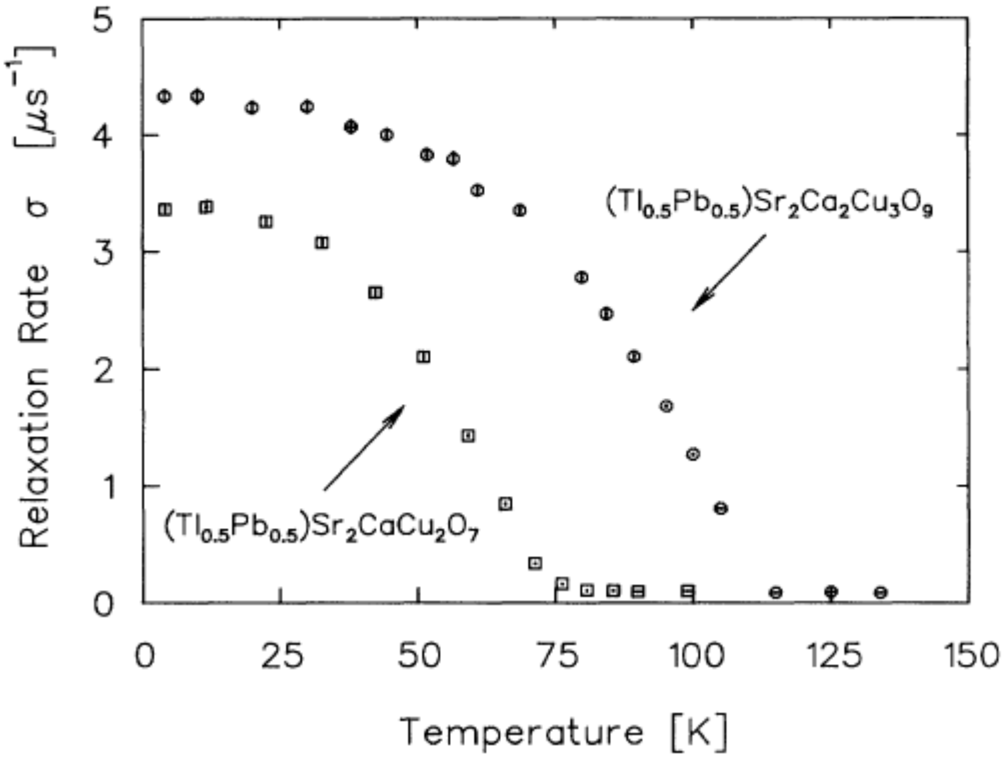


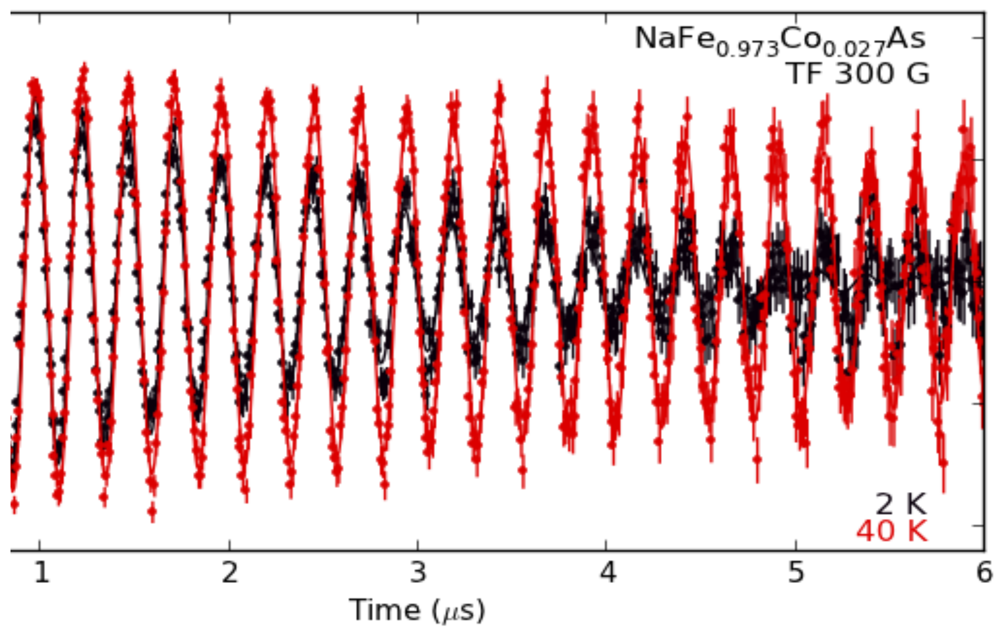

A. Savici, http://neutron.magnet.fsu.edu/muon_relax.html

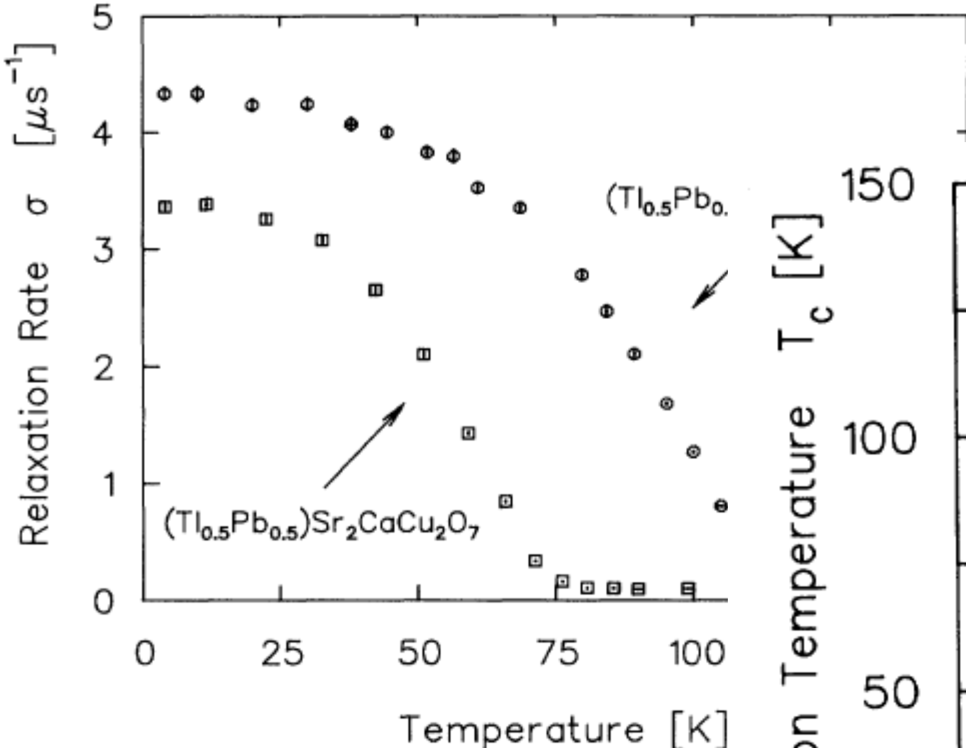
# Inhomogeneous magnetism probed by µSR: e.g., superconductivity

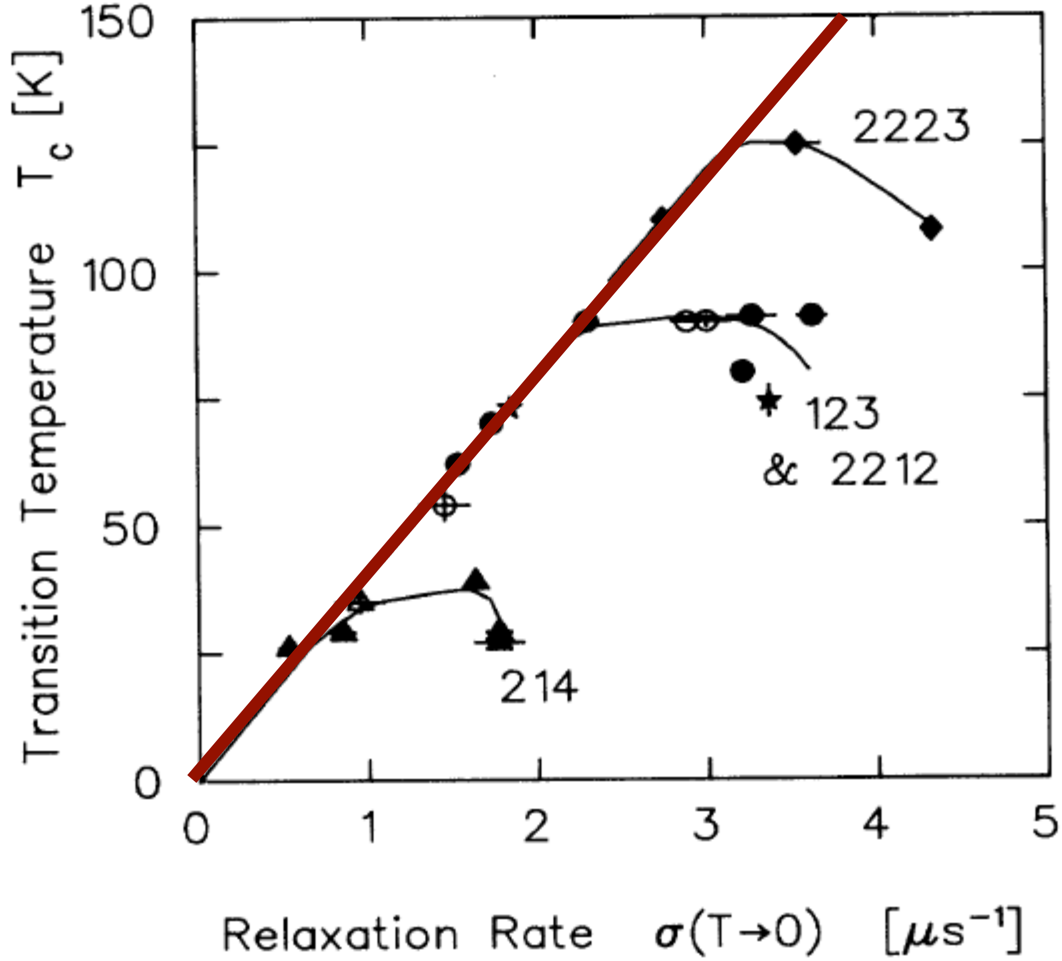










- Uemura et al., PRL 1988 => “Uemura Plot”

# Why do we love Muons

- They are a LOCAL probe of the magnetic field in a material:
  - Highly complementary to other probes of local atomic and electronic structure from scattering and STM

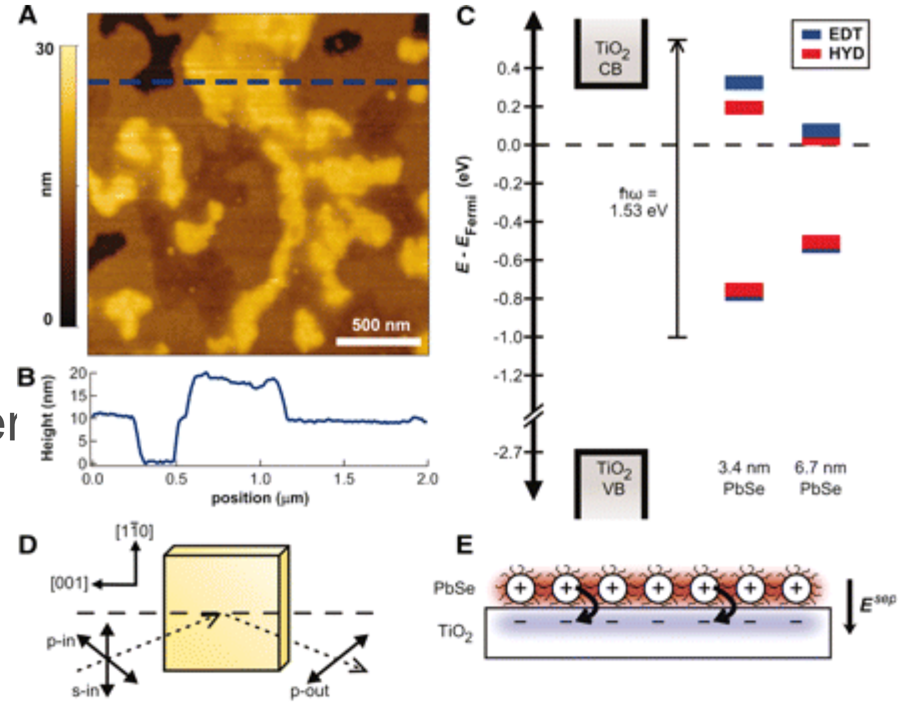
A very versatile probe of magnetism in complex materials

# Why are muon experiments not more ubiquitous

- ~~Very difficult to do the experiments?~~
- ~~Very difficult to analyze the data?~~
- ~~Many different and easier ways of getting the same information?~~
- Scarsity of muons!
  - CMMS continuous source at TRIUMF in Vancouver, Canada
  - ISIS Pulsed Muon Facility, UK
  - Paul Scherrer Institute Muon Facility, Switzerland
  - RIKEN-RAL Muon Facility, Japan

# Complex materials

- Photovoltaics with improved efficiency
  - Nanoparticles in the light collecting layer
- High energy density batteries and fuel cells
  - Electrodes
  - Electrolytes
  - Catalysts
- Electrical transport
  - High temperature superconductors
- Next generation electronics
  - Spintronics
  - Multiferroics



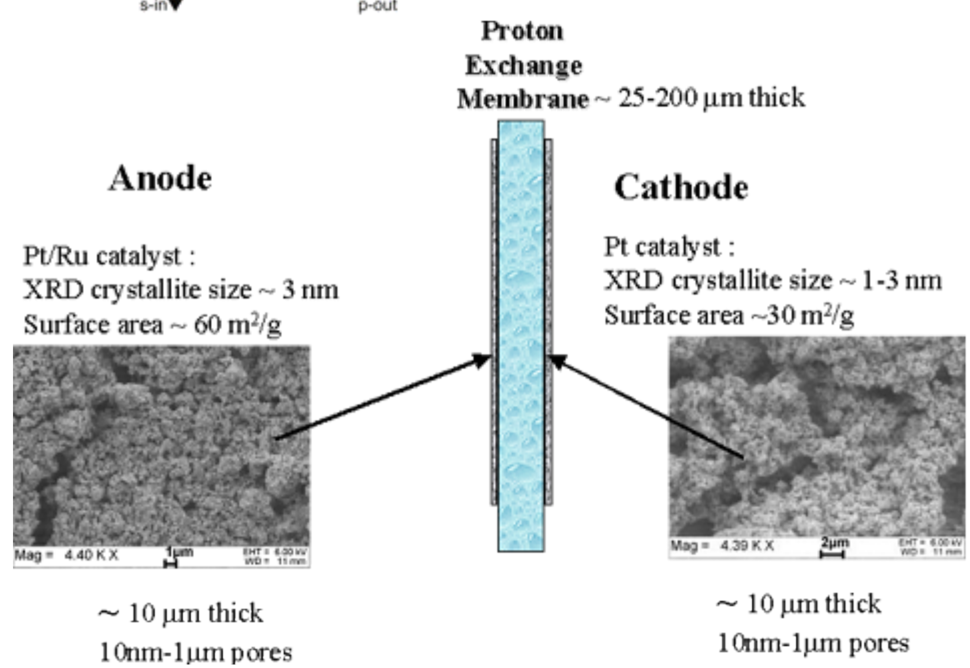




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Image credits: 10.1126/science.1185509
U. Uppsala

# Materials with colossal emergent properties close to a metal-insulator transition

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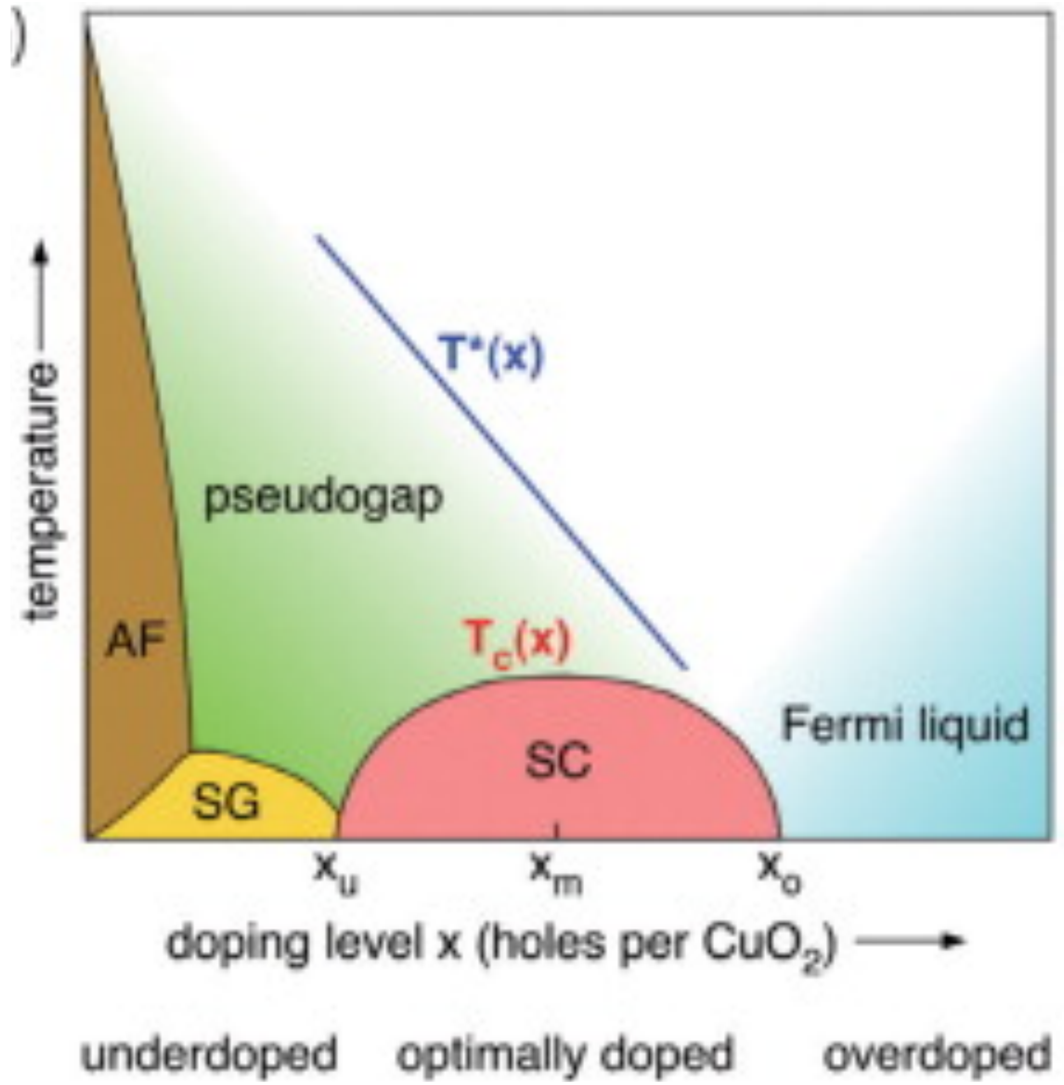
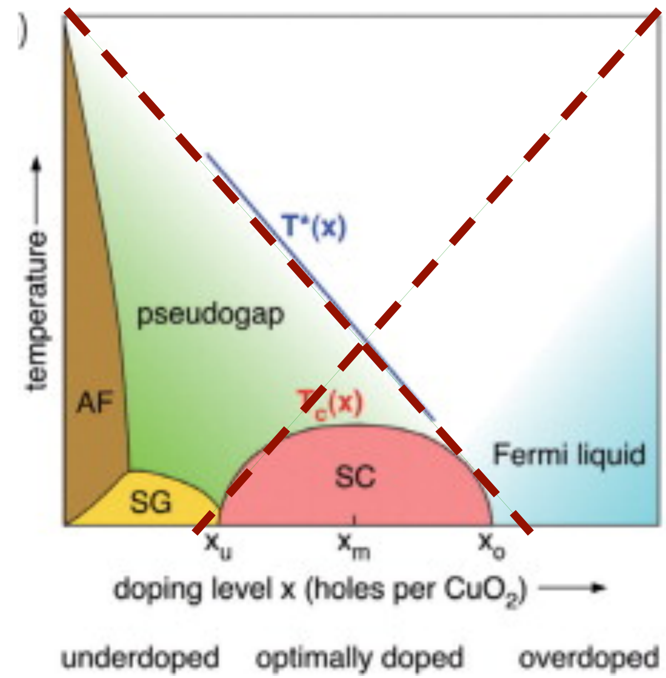



Generic high temperature superconducting cuprate phase diagram

Annette Bussman-Holder and K. A. Muller 2008 review

## Cuprate Superconductivity

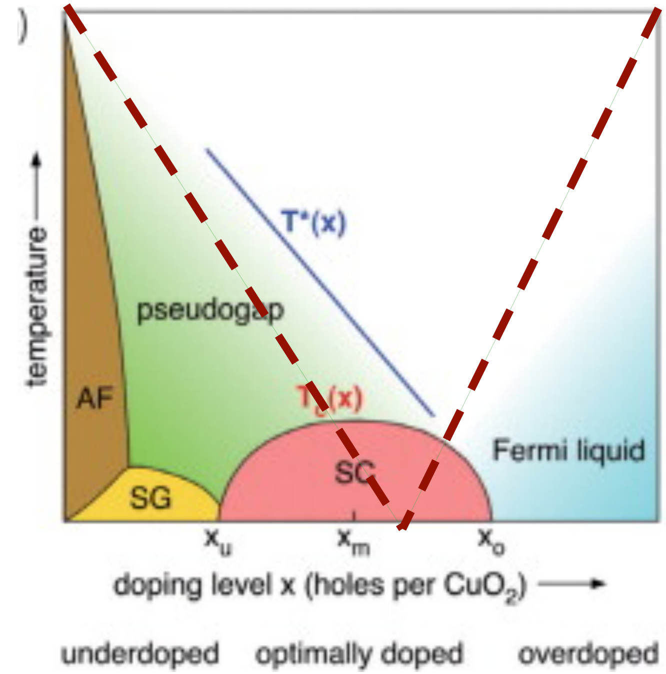
- Basic picture of doped, half-filled Mott insulator
- Antiferromagnetism and spin fluctuations
- Strange metal
- Spin gap -> pseudogap
- Is it an X or a V?




Generic cuprate phase diagram
Bussman-Holder and Muller 2008 review

# Cuprate Superconductivity

- Basic picture of doped, half-filled Mott insulator
- Antiferromagnetism and spin fluctuations
- Strange metal
- Spin gap -> pseudogap
- Is it an X or a V?
- Nanoscale electronic inhomogeneities (stripes)
  - Really hard to see!  Took 8 years to find them in LBCO
  - Took 10 more years to find them in BSSCO (controversial STM results)
  - Took 7 more years to find them in YBCO (less controversial resonant scattering)




Generic cuprate phase diagram
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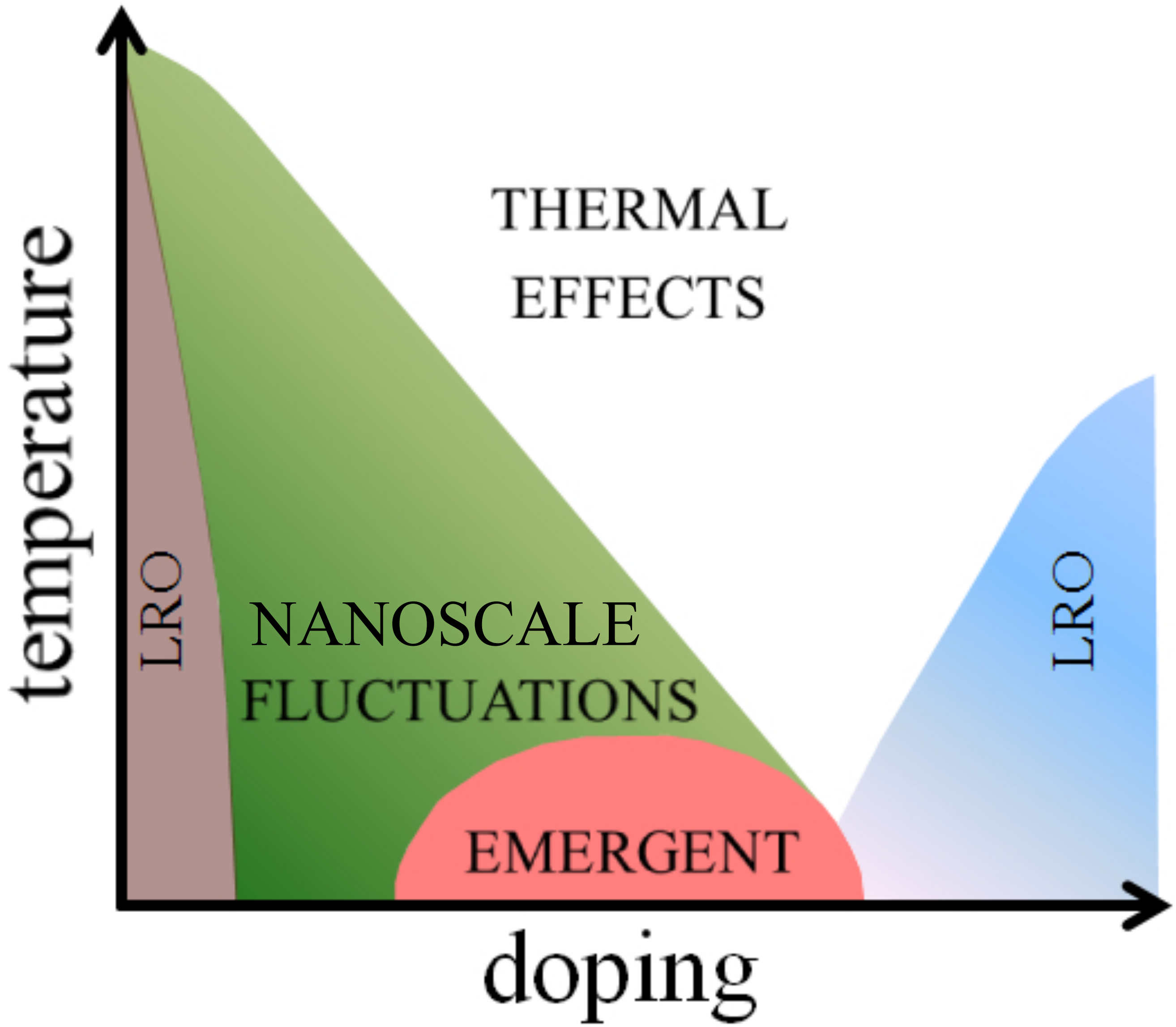



An even more generic phase diagram?????

# Materials with colossal emergent properties close to a metal-insulator transition

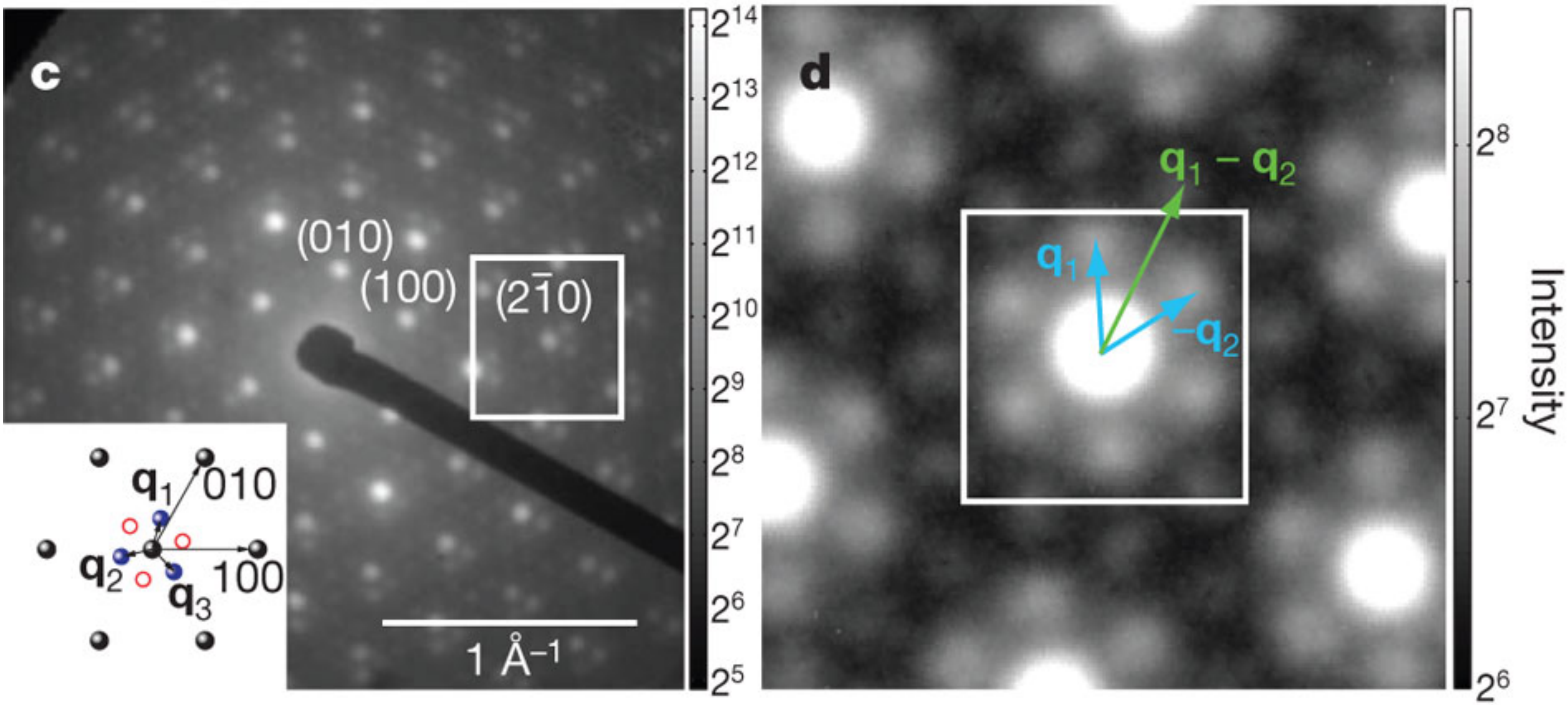
1. How can we detect and measure *LOCAL* broken symmetry electronic states in materials?

2. How ubiquitous are they?

3. How important are they?

# How do we detect a global broken symmetry state?

- New Bragg Peaks! E.g., CDW in 1T-$TaS_2$
- Eichberger etal Nature **468**, 799–802 (2010) doi:10.1038/nature09539
- Accompanying changes in transport/susceptibility/spectroscopy



# What happens if the broken symmetry state is only *short-range ordered*?

- Signal from the broken symmetry state is becomes diffuse
- Need a probe of local correlations
- Need to look for signals in measures of disorder in the material

Competition

+

Disorder (static or entropic)

Nanoscale Fluctuations and Heterogeneities

?

Emergent Properties

# How can local broken symmetries hide?

# How are hidden local broken symmetries revealed?
# #1: direct imaging

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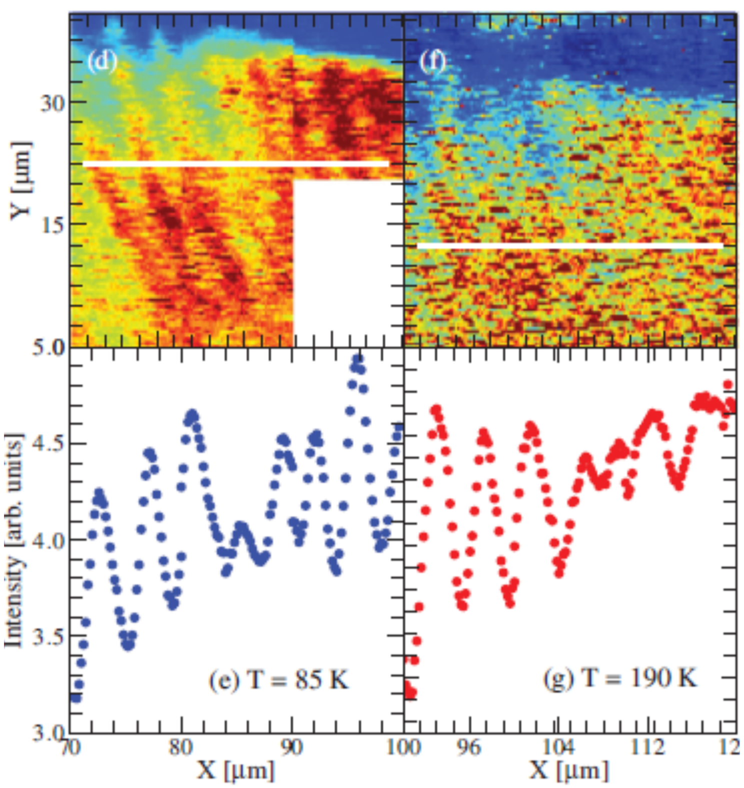
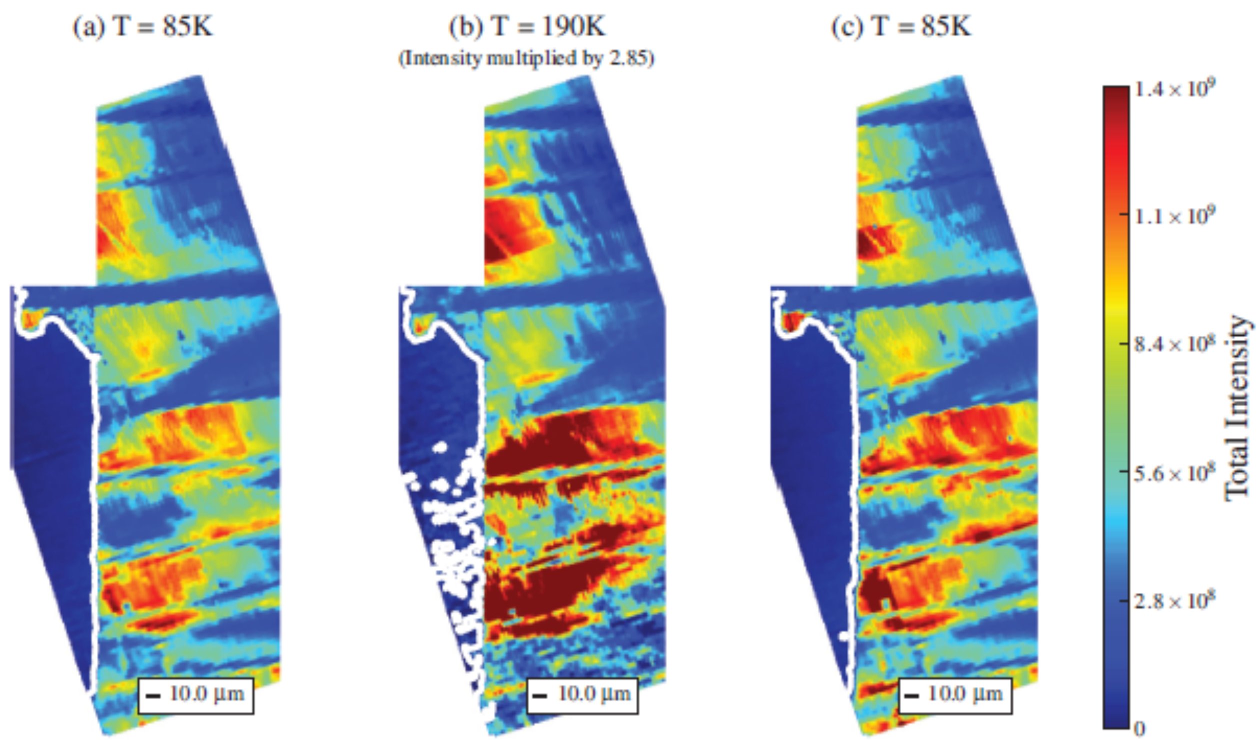
# Scientific Highlights: Nanoscale AF texture in manganites

- First spatially resolved images of nanoscale antiferromagnet texture using resonant soft x-ray scattering (PRB 2013)
- Applied to layered manganite materials

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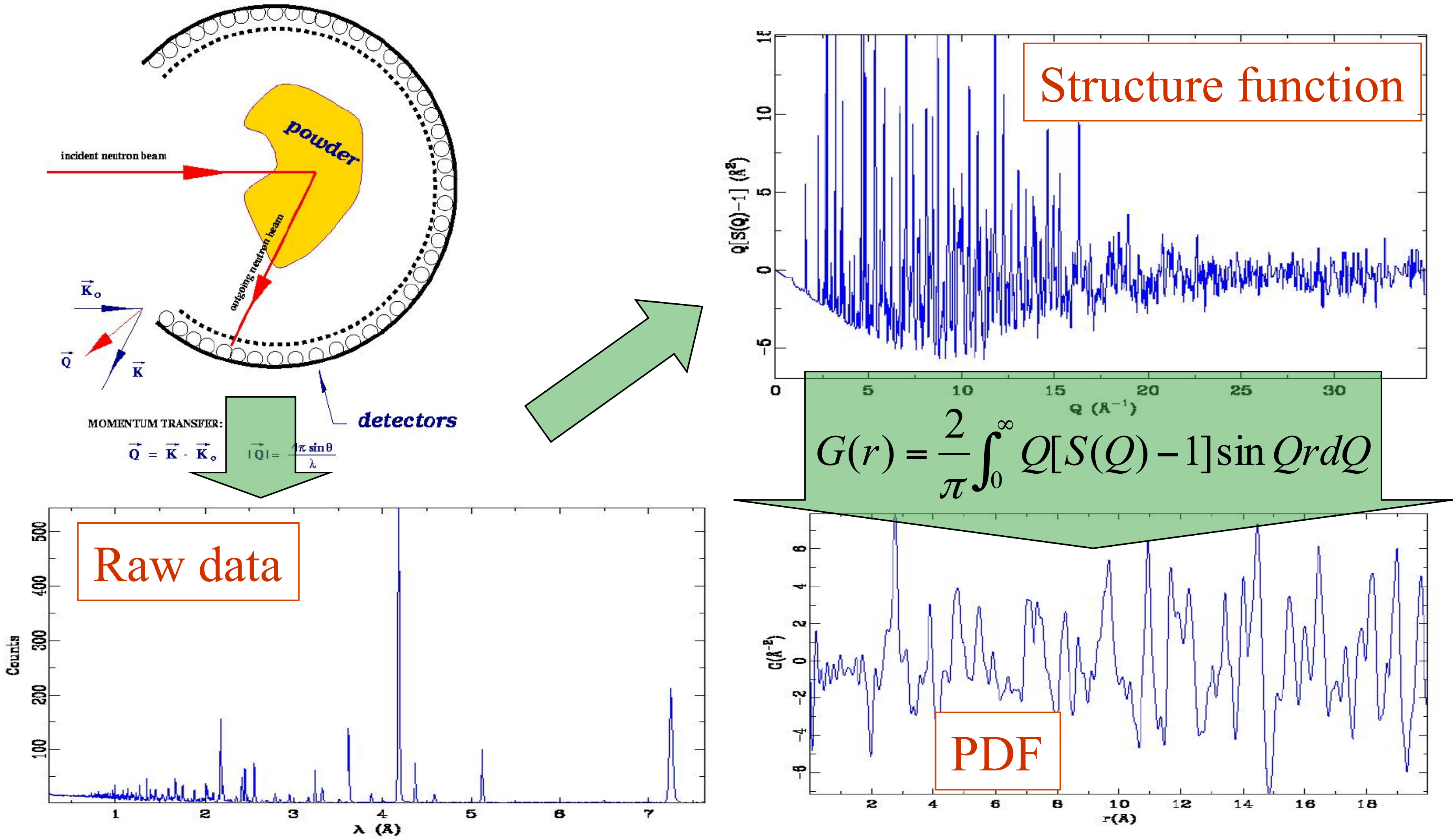
# How are hidden local broken symmetries revealed?
# #2 Studies of local structure/correlations

# Obtaining the PDF




$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr\,dQ$$

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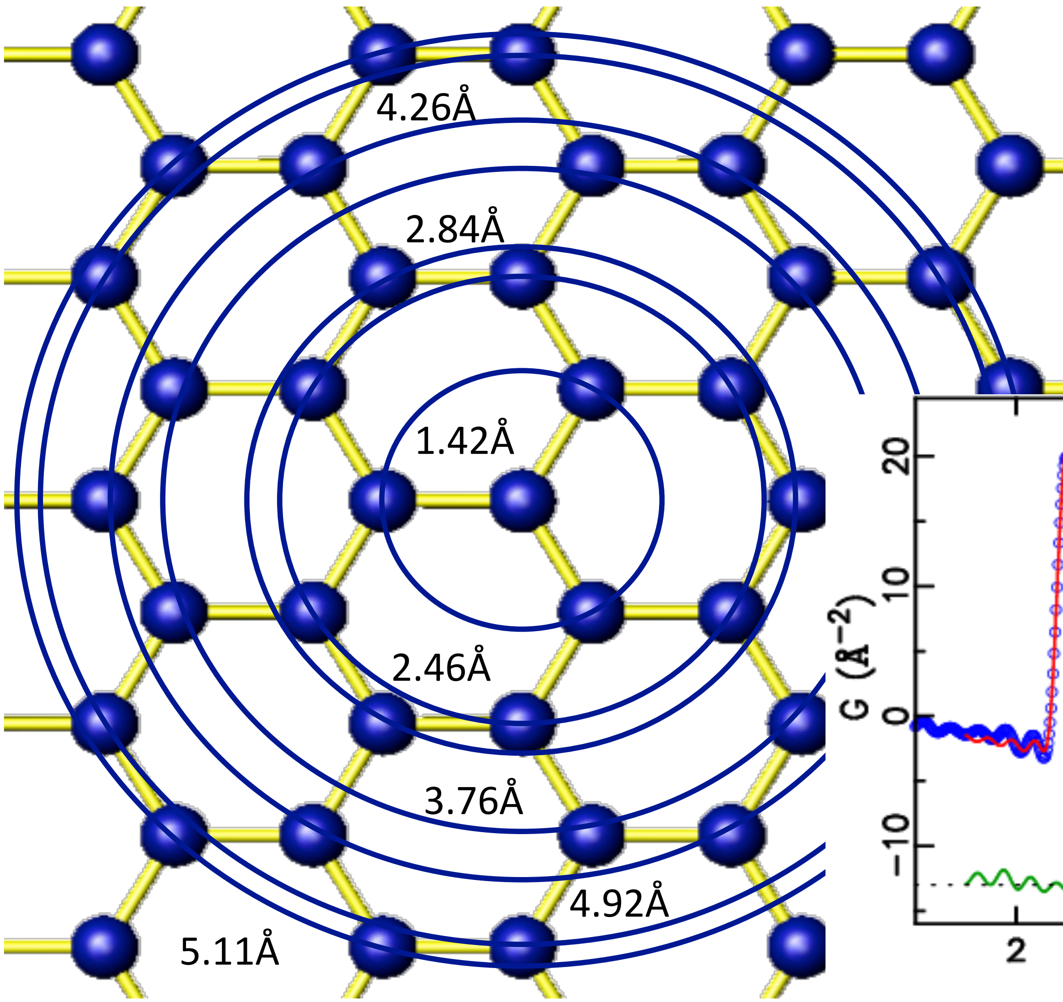
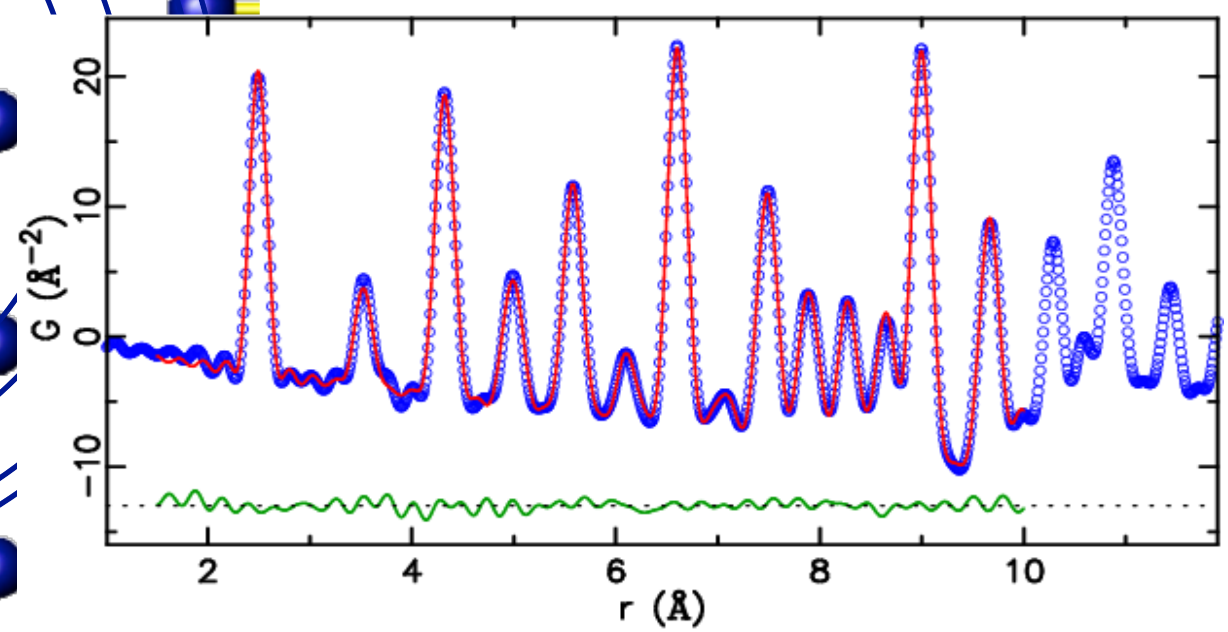
# Nanostructure refinement



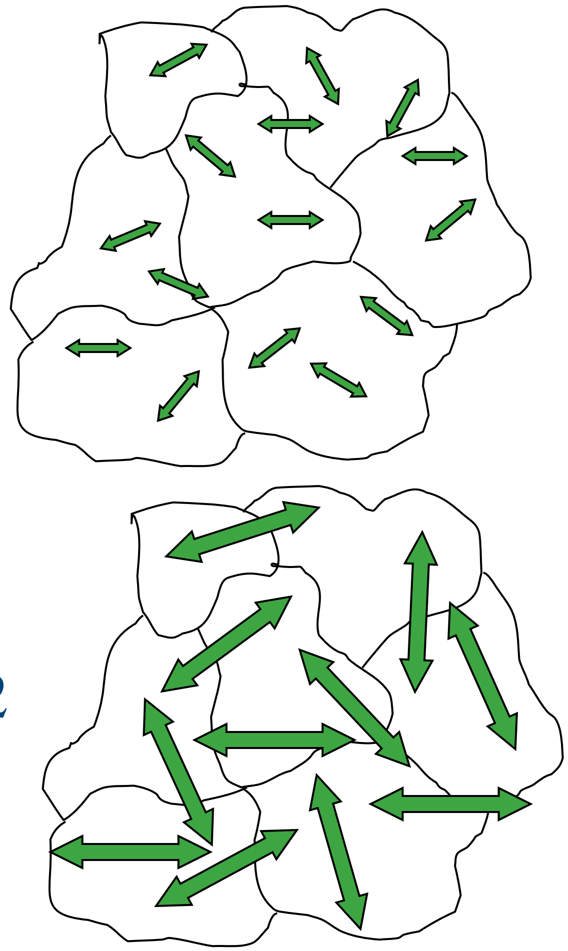

Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.

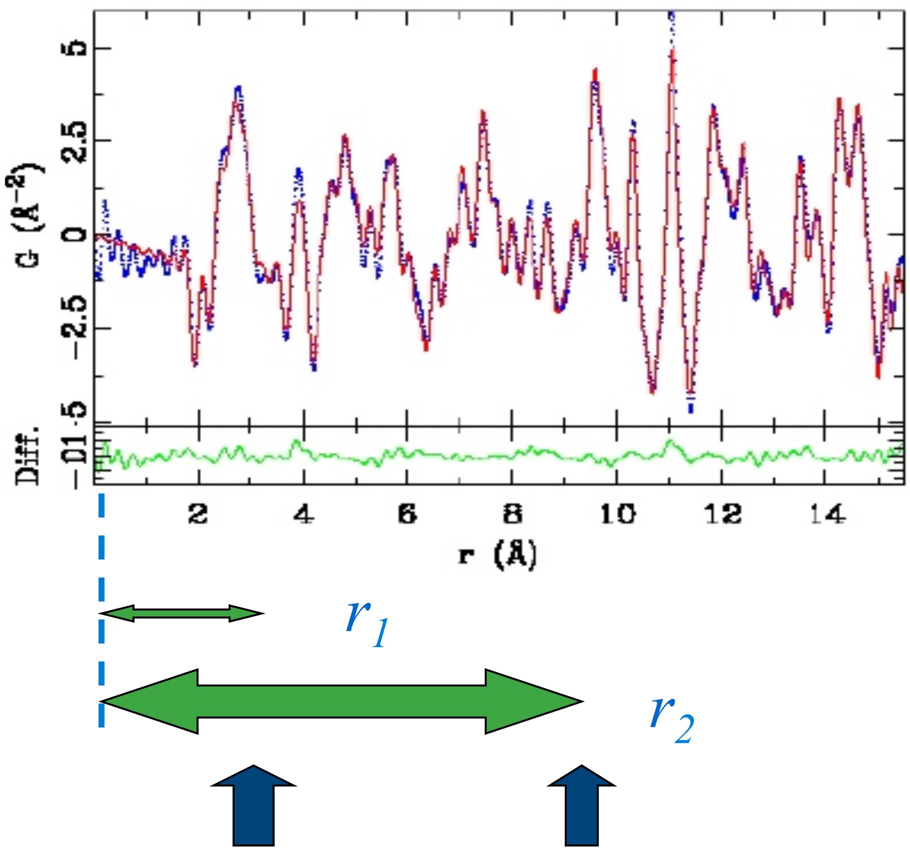


# Observing Nanodomains in the PDF

$r_1 << \xi$

$r_2 \sim \xi/2$

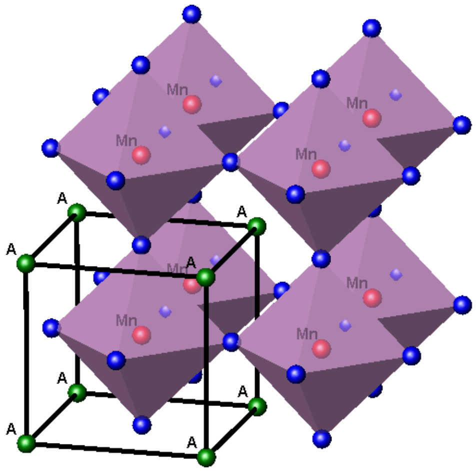


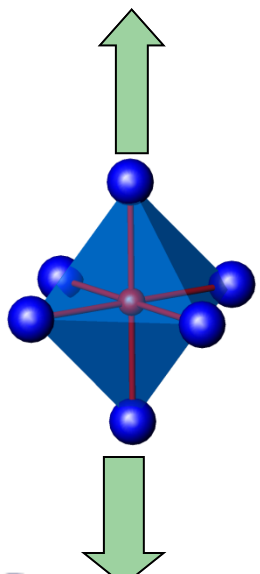


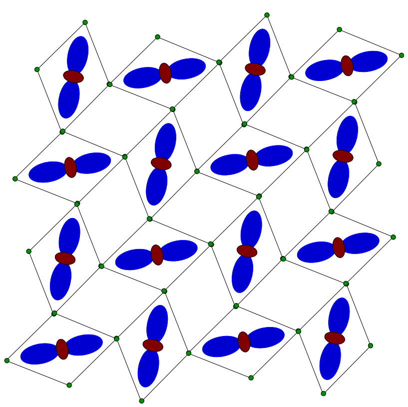

Intra-domain structure

Inter-domain structure

# How is PDF sensitive to MI transition?



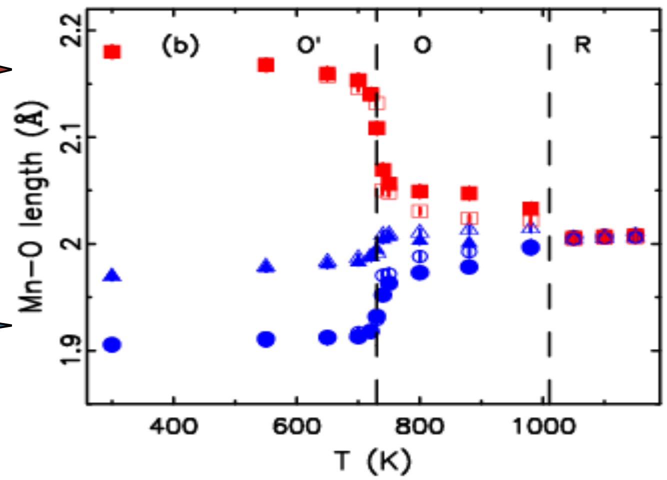


- $Mn^{3+}$: JT distorted octahedra:
  - 4 x ~1.94 A Mn-O bonds
  - 2 x 2.17 A Mn-O bonds
  - $R_{long}$-$R_{short}$ = 0.23A
  - 8 long and 4 short O-O distances centered around 2.75A
- $Mn^{4+}$: undistorted octahedra:
  - 6 x ~1.94 A Mn-O bonds
- Delocalized holes: undistorted octahedra:
  - 6 x ~1.94 A Mn-O bonds

# T-depence of Mn-O bond distribution

Long-bonds

Short-bonds




Average structure

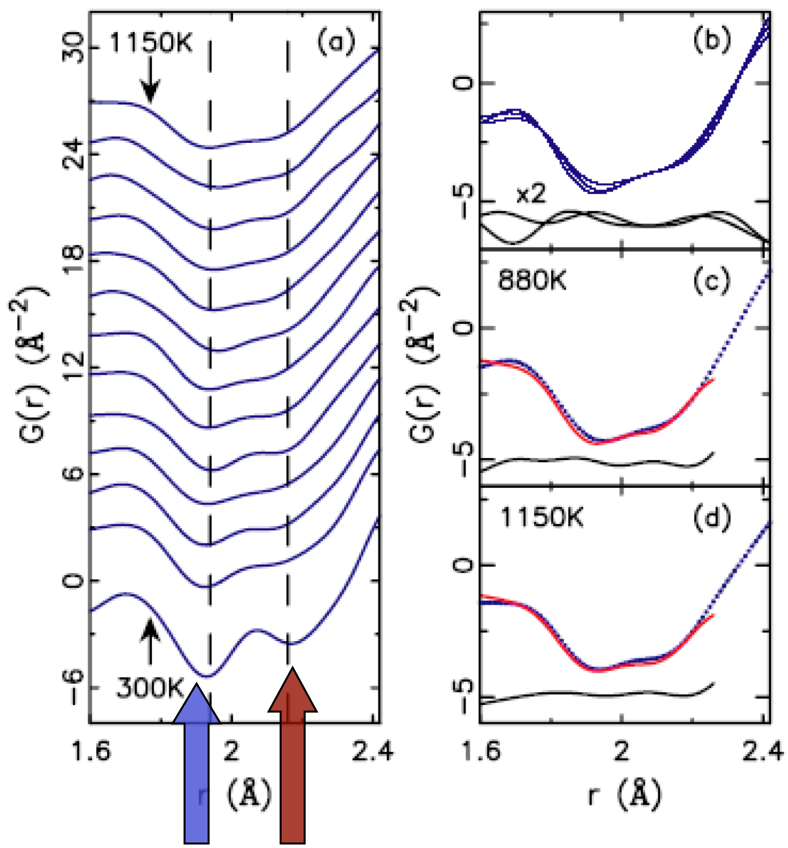
- Mn-O bond lengths are invariant with temperature, right up into the R-phase

JT distortions persist locally in the pseudocubic phase

Xiangyun Qiu, Th. Proffen, J. F. Mitchell and S. J. L. Billinge, *Phys. Rev. Lett.* **94**, 177203 (2005).

Agrees with XAFS result: M. C. Sanchez et al., PRL (2003).

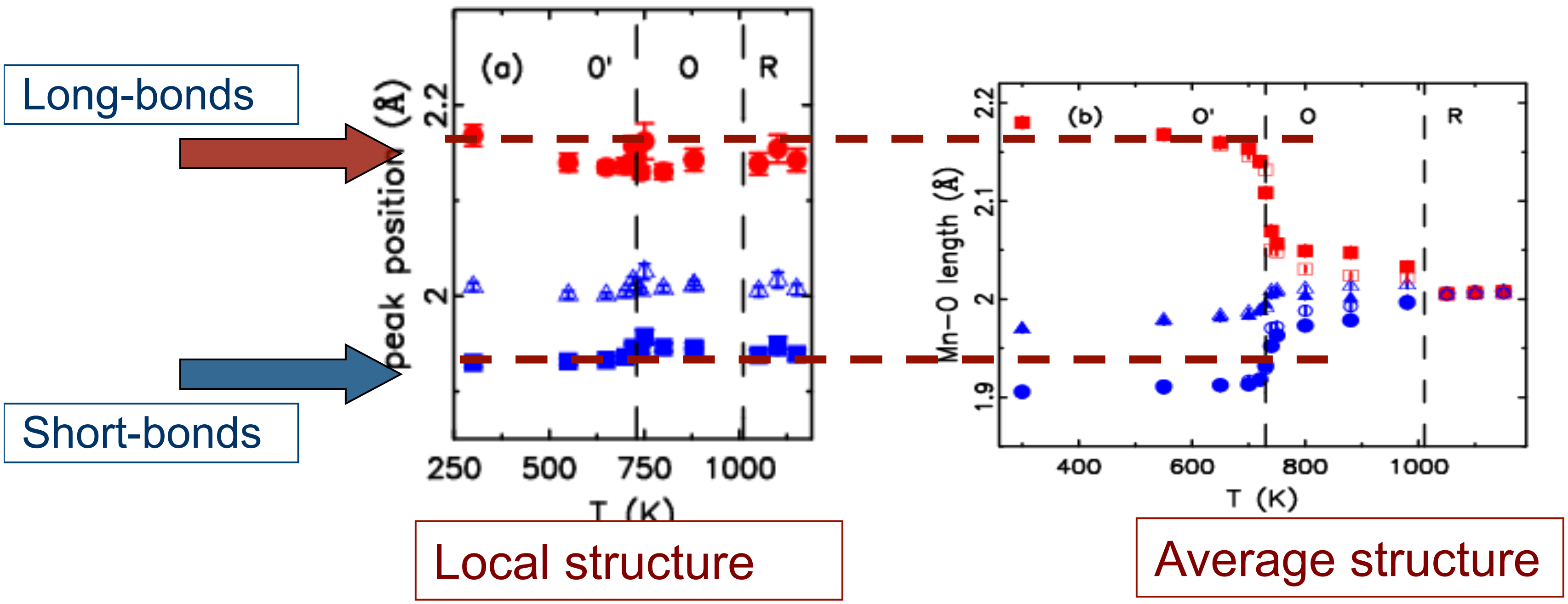
# Example: orbitally disordered phase in $La_{1-x}Ca_xMnO_3$




Local structure: JT distorted
Average structure: no JT distortion
=> Domains of local JT order

From Qui X., Proffen Th., Mitchell J. and Billinge S.J.L. PRL, 94, 177203 (2005).

# T-depence of Mn-O bond distribution

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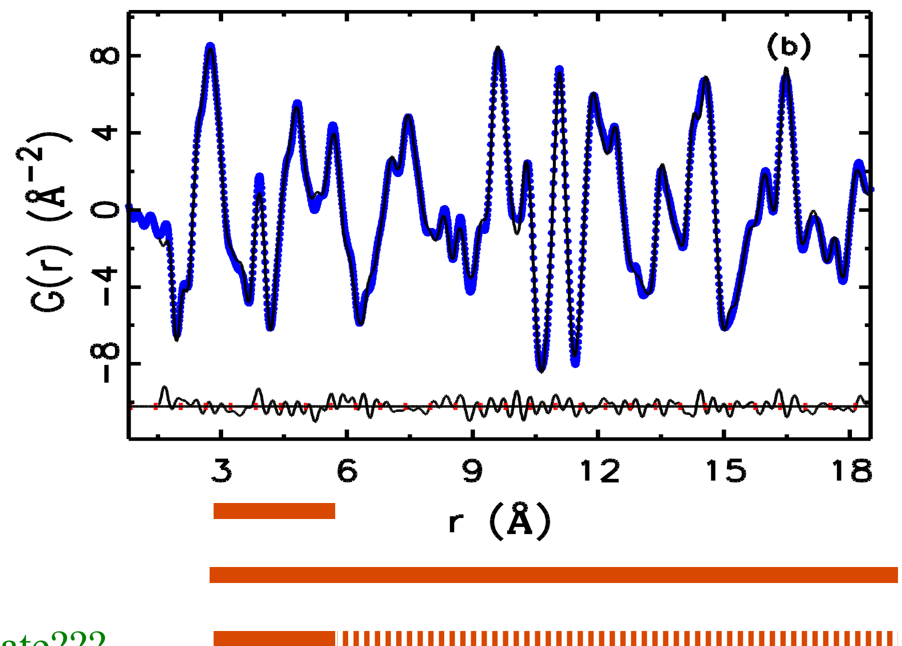
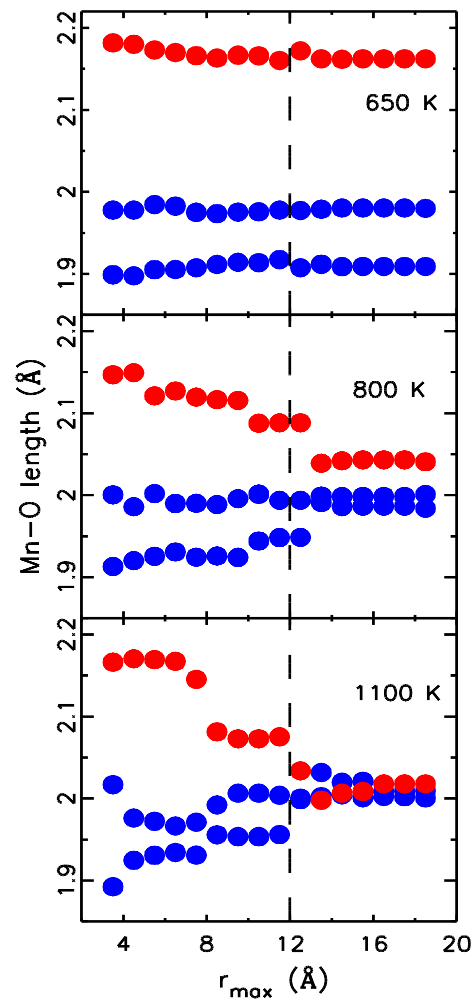
# Crossover from local to average structure




Local

Average

Intermediate???



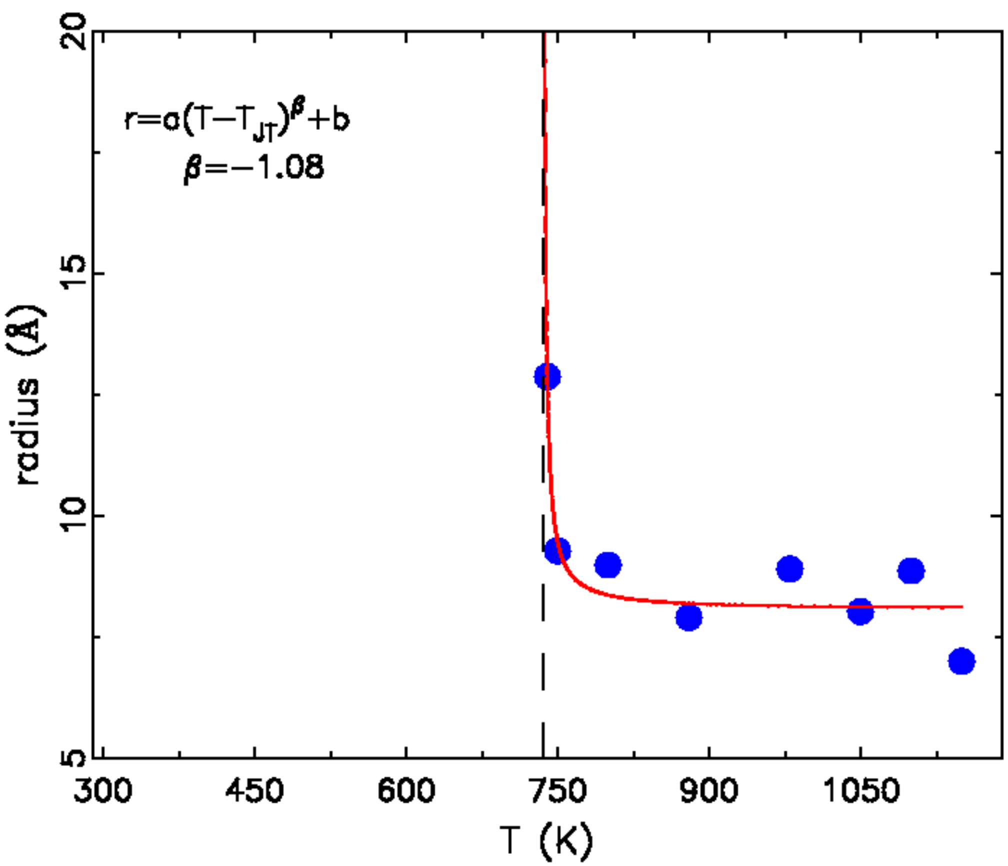

O

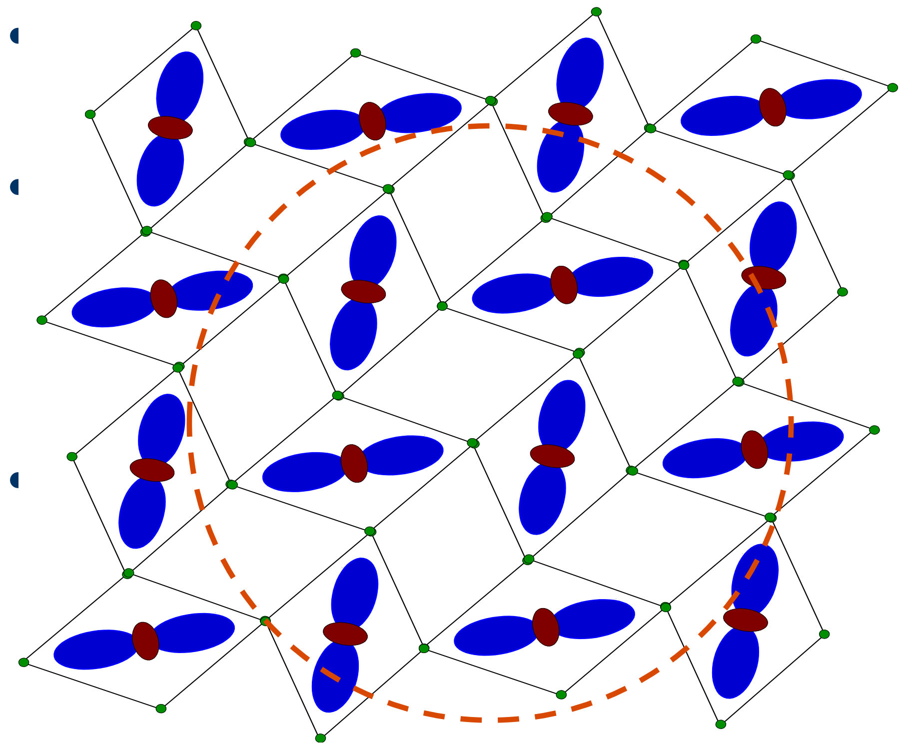
O'

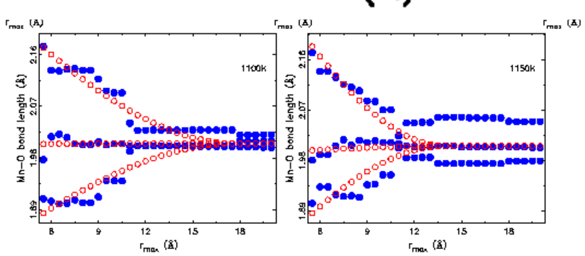
R

- Varying range refinement
  - Fix $r_{min}$
  - Vary $r_{max}$
  - x axis is $r_{max}$

# R-dependent fits vs T

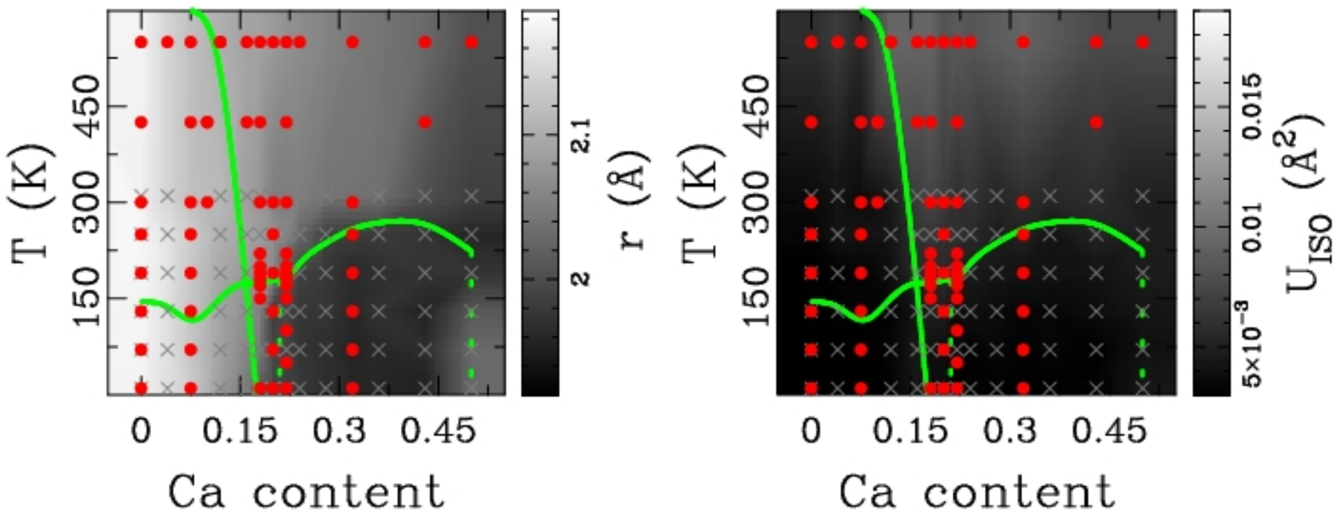




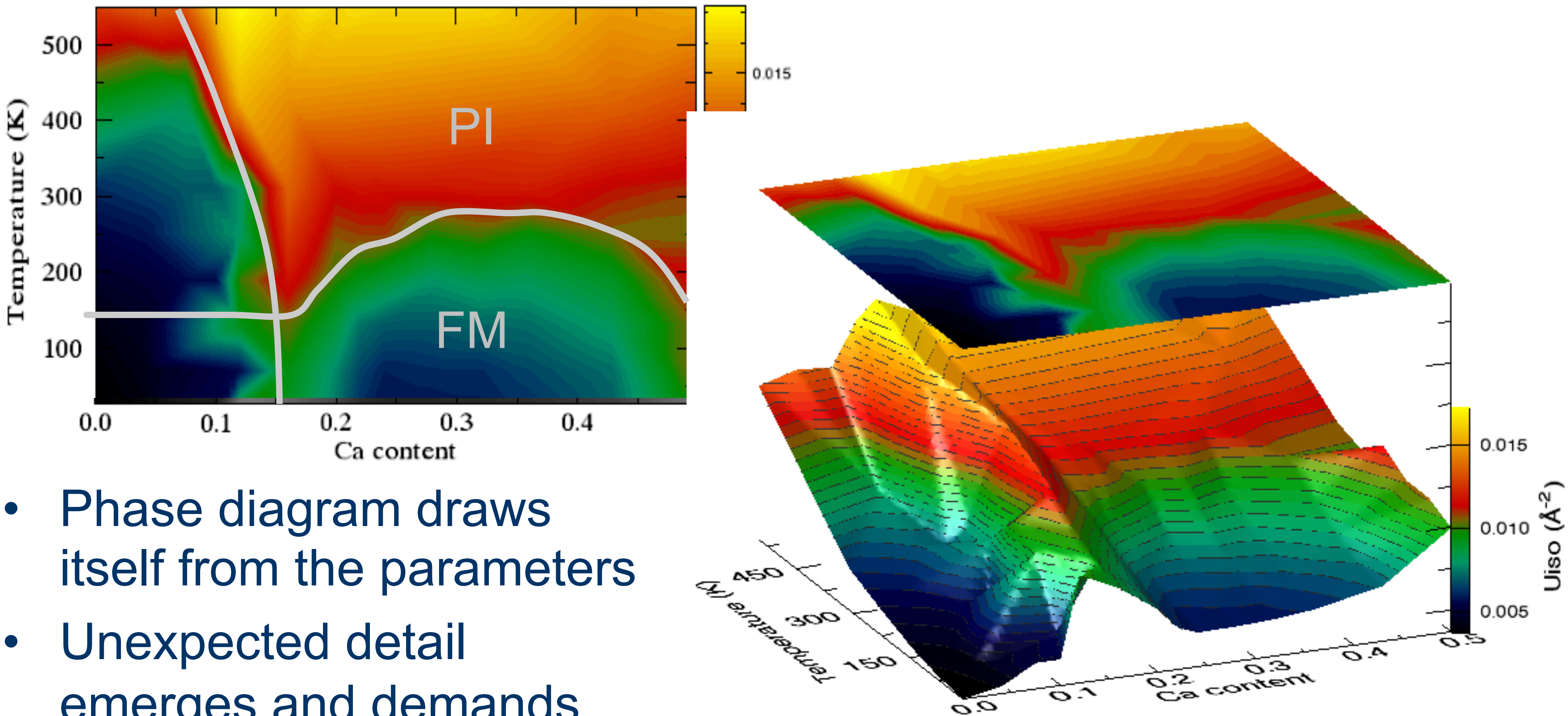

$$f\left(r,d\right)=\left[1-\frac{3r}{2d}+\frac{1}{2}\left(\frac{r}{d}\right)^{3}\right]\Theta(d-r)$$

# $La_{1-x}Ca_xMnO_3$ and colossal magnetoresistance



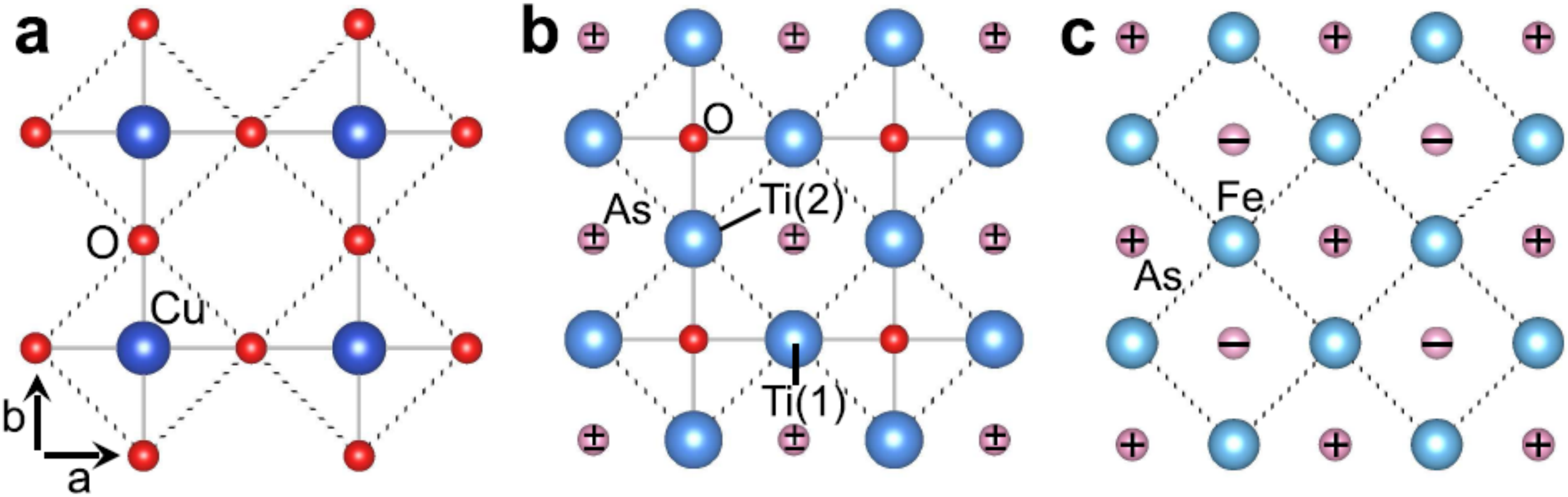

- Key point is that understand colossal magnetoresistance, we need many data points throughout the phase diagram.
- High throughput local structural studies!

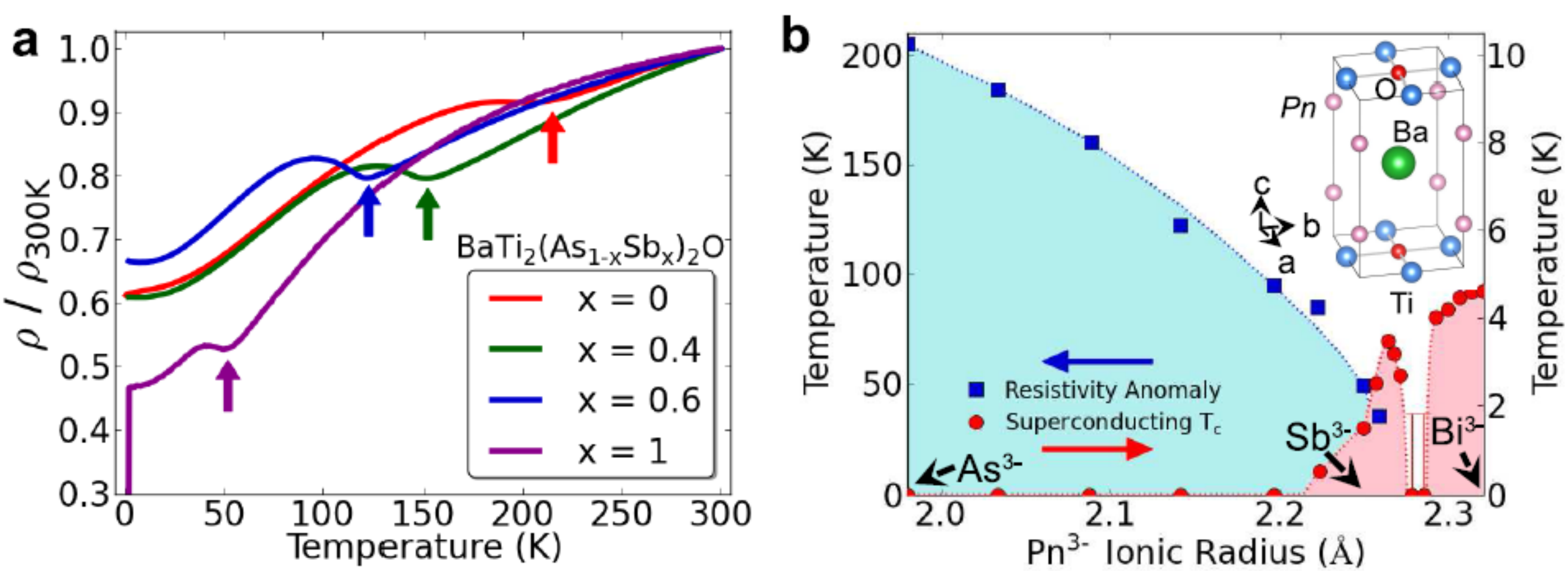
# Remarkable dataset: Phase diagram emerges from single refined parameters



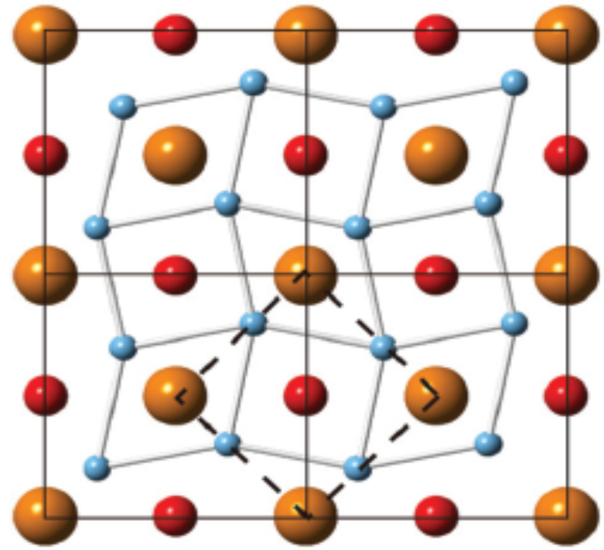

- Phase diagram draws itself from the parameters
- Unexpected detail emerges and demands interpretation

# $BaTi_2Pn_2O$ ($Pn$ = As. Sb. Bi)



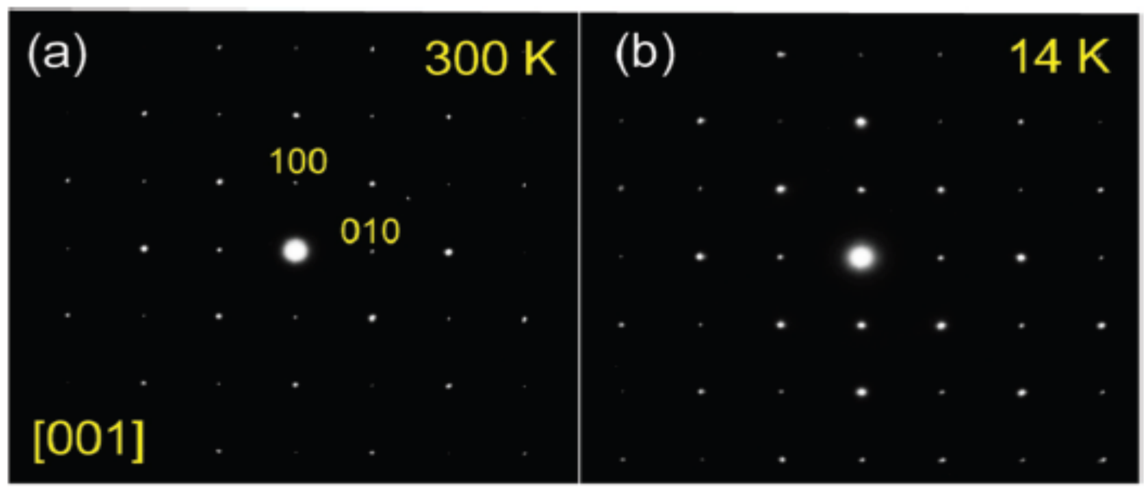



# Searching for the CDW



Proposed CDW distortion due to unstable phonon mode calculated from first principles (Subedi, PRB 87: 054506 (2013))

Observed electron diffraction patterns from $BaTi_2Sb_2O$ and $BaTi_2As_2O$: no superlattice peaks!

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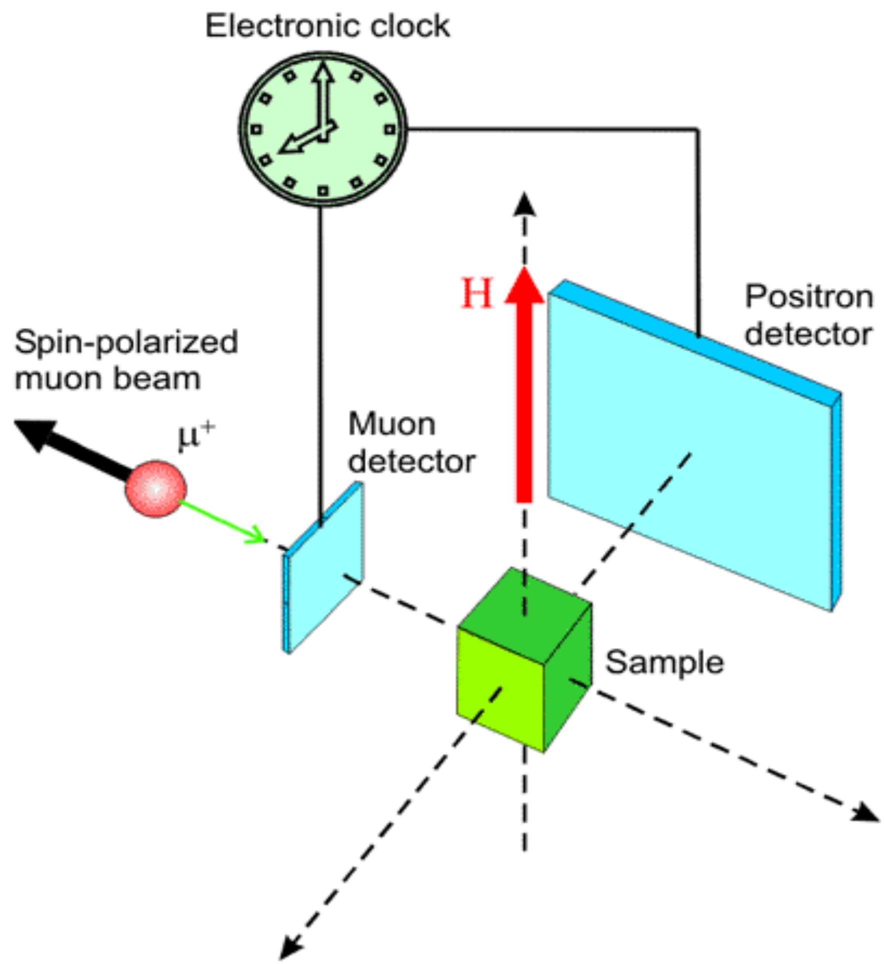
# Probing magnetism with zero-field μSR



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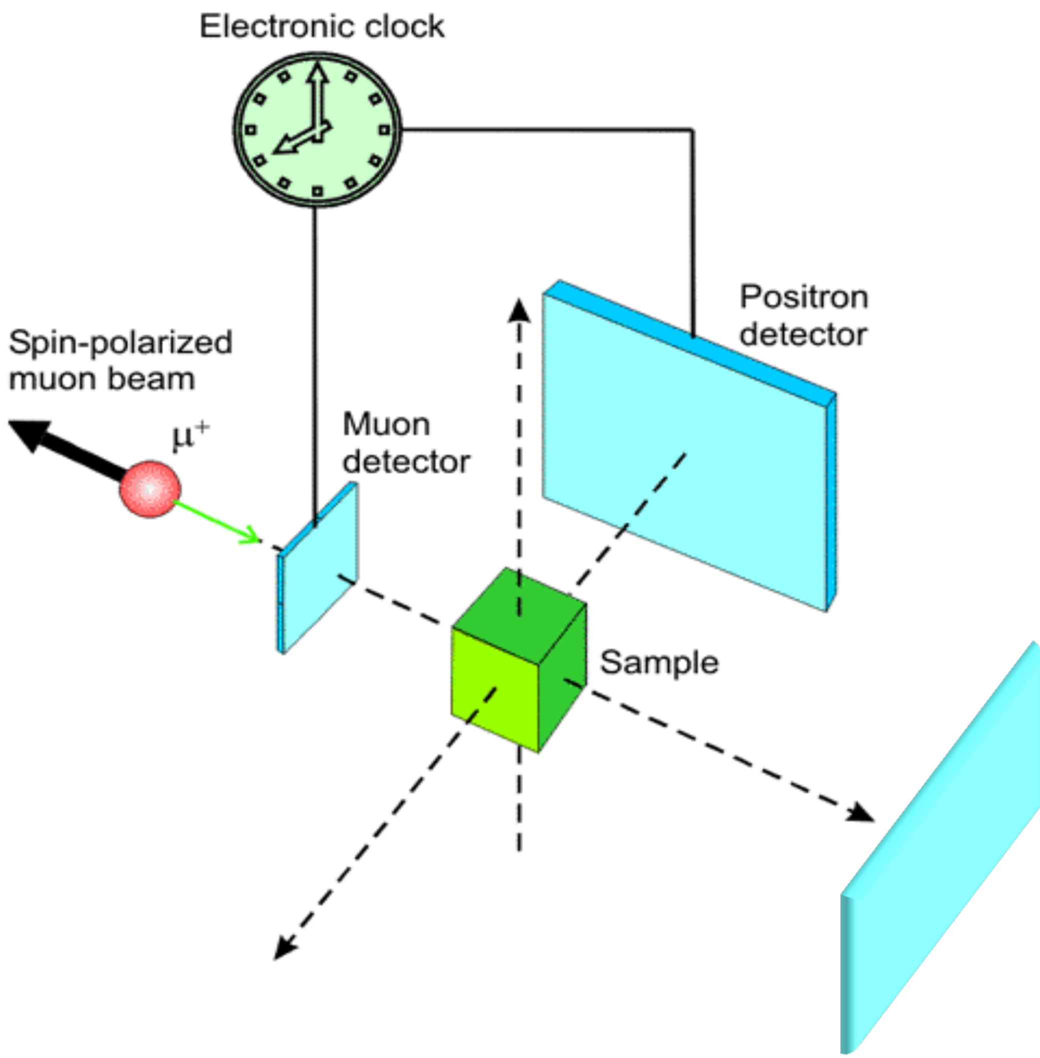


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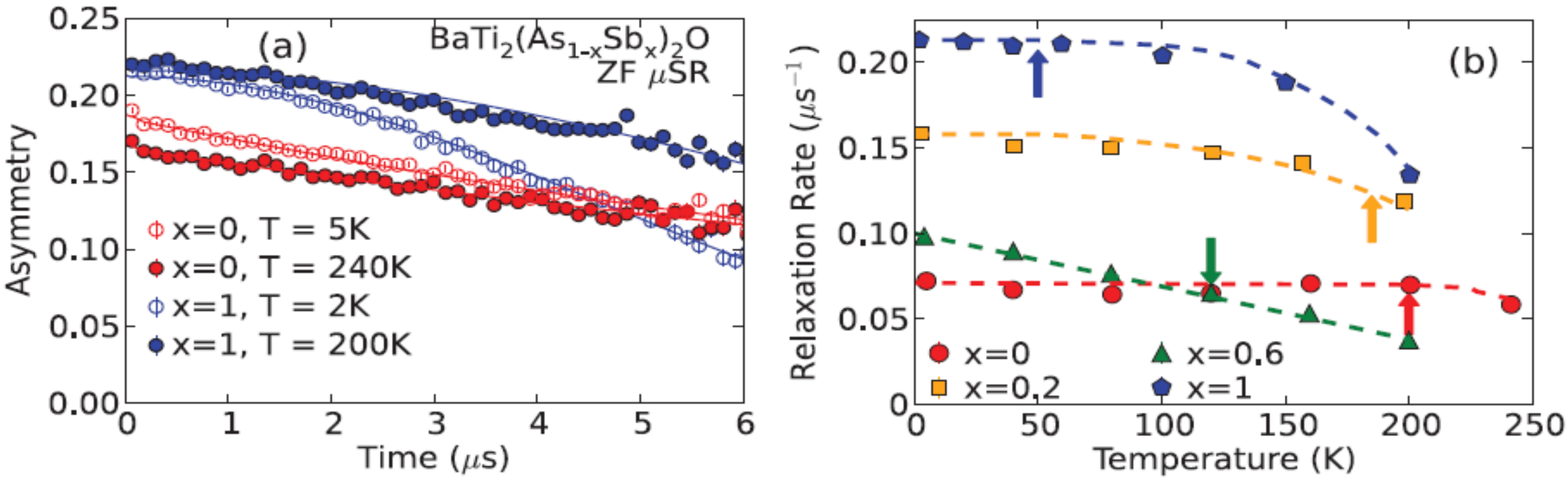
# Magnetic order probed by μSR

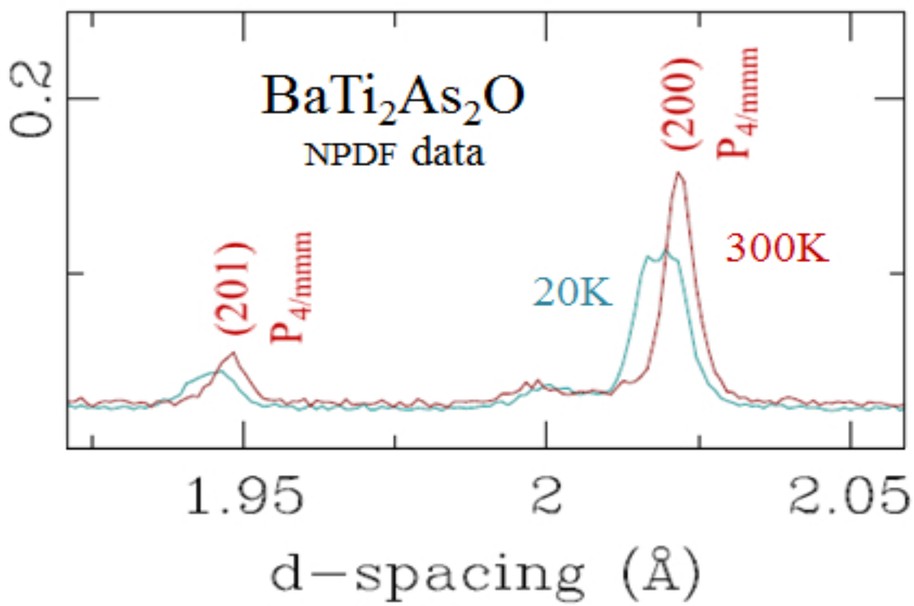


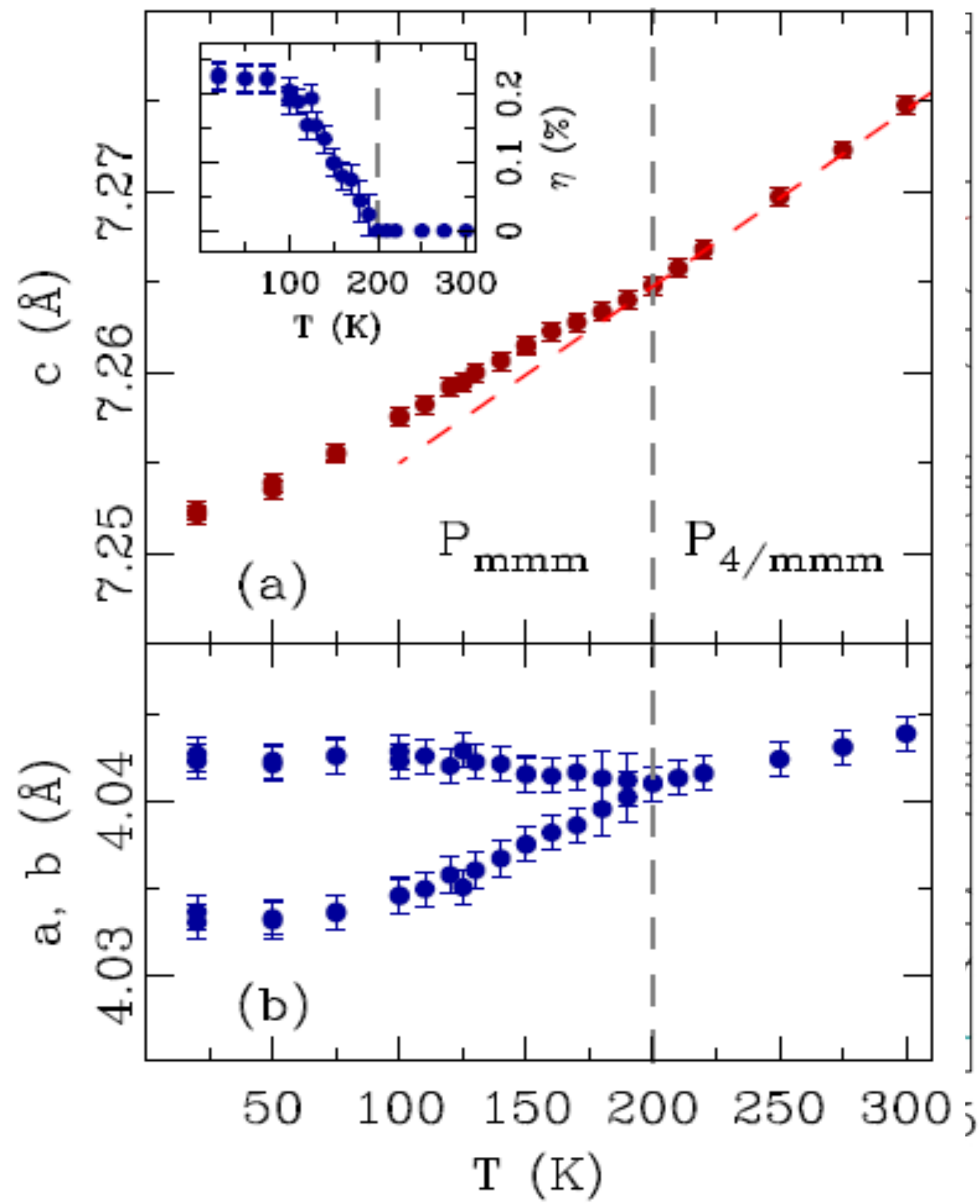

Y. Nozaki et al. PRB 88 214506 (2013)

Lack of increase in relaxation rate at density-wave temperature indicates no magnetic order

Conclusion: No SDW in $BaTi_2(As,Sb)_2O$

# Result is (probably) nematic charge order




Subtle but observable orthorhombic splitting of (200) and (201) peaks starting below approximately 200 K

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# Case study #2: Dimers in $CuIr_2S_4$

Why is it interesting?

1. Frustration

2. Metal-insulator transitions

3. Carrier localization and broken symmetry states at low-temperature

4. Signal from broken symmetry state is large (colossal)!

# $CuIr_2S_4$, Why is it interesting?

1. Frustration

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# Spinel structure

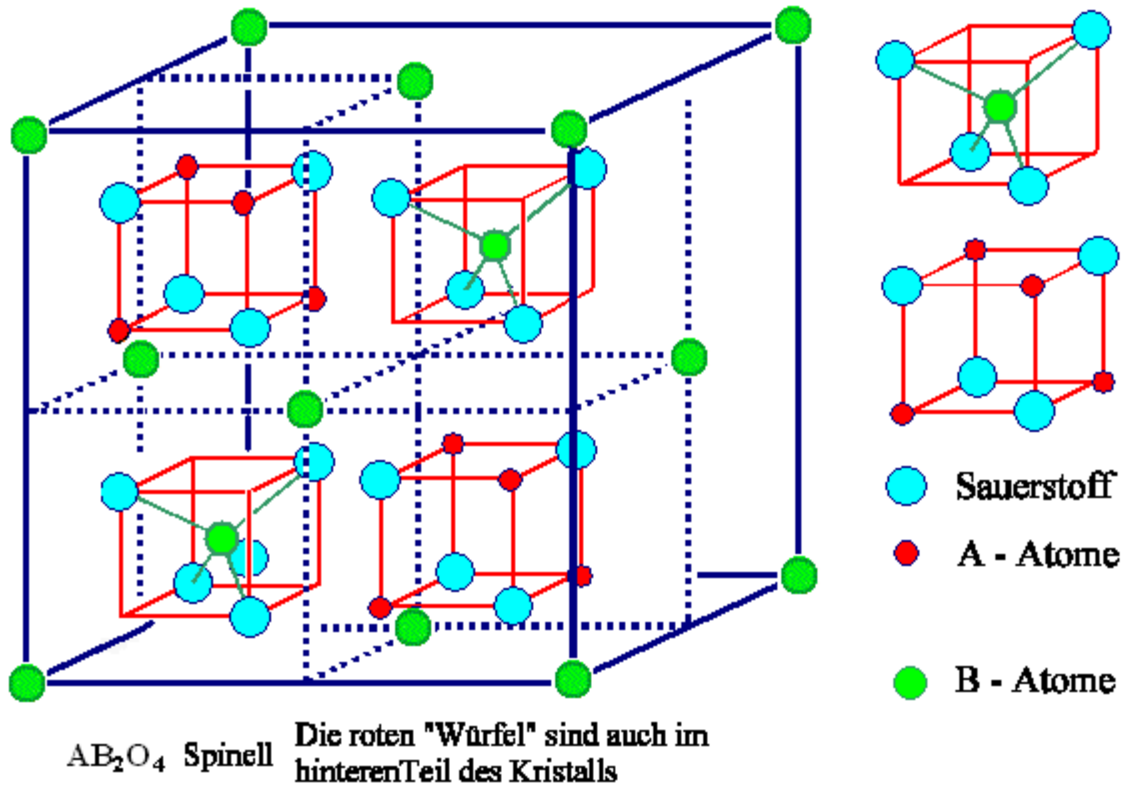
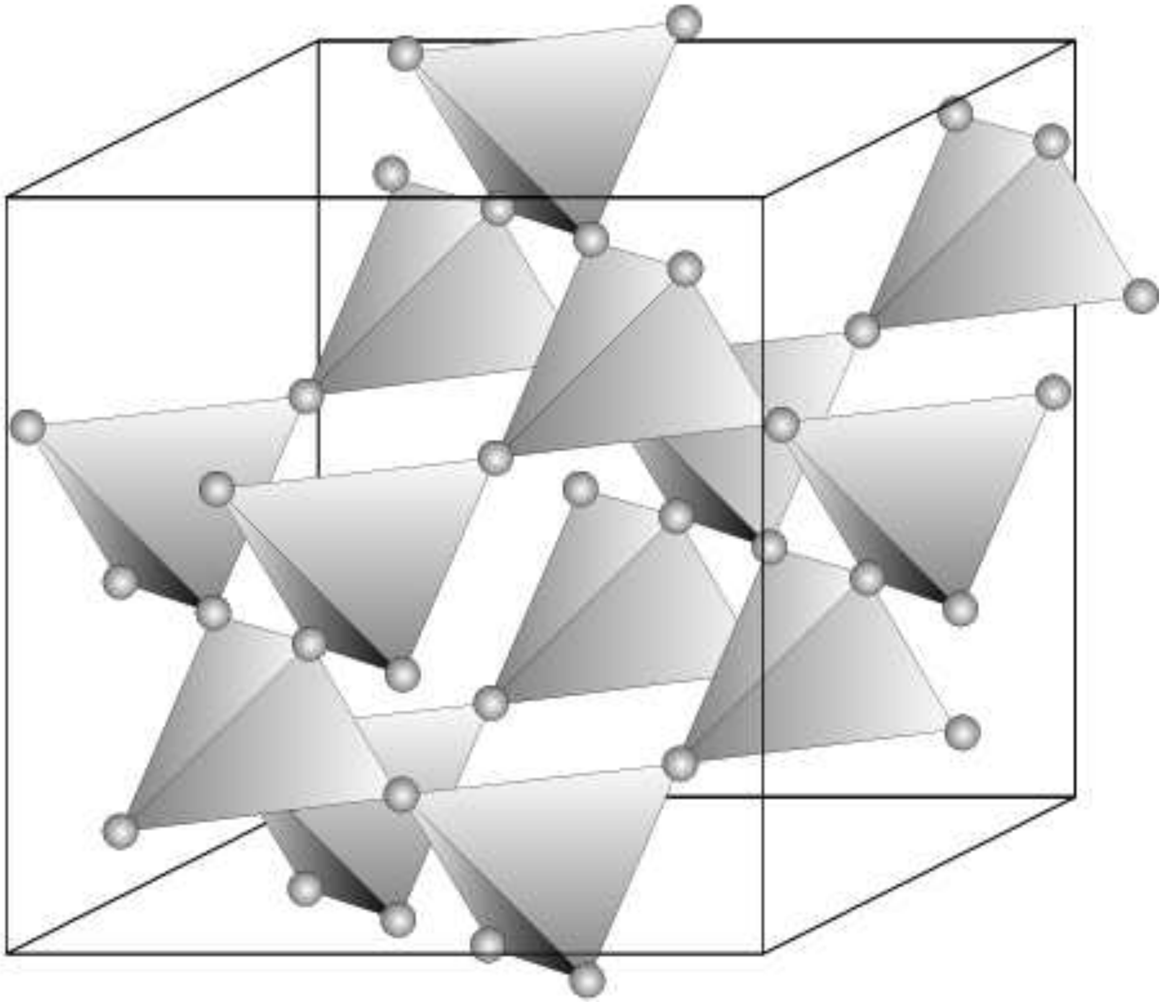
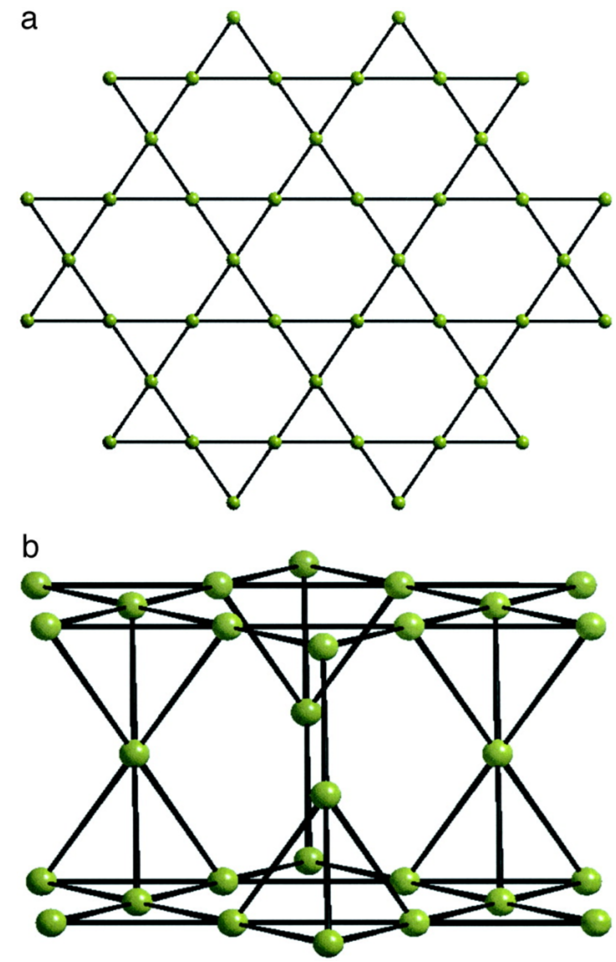


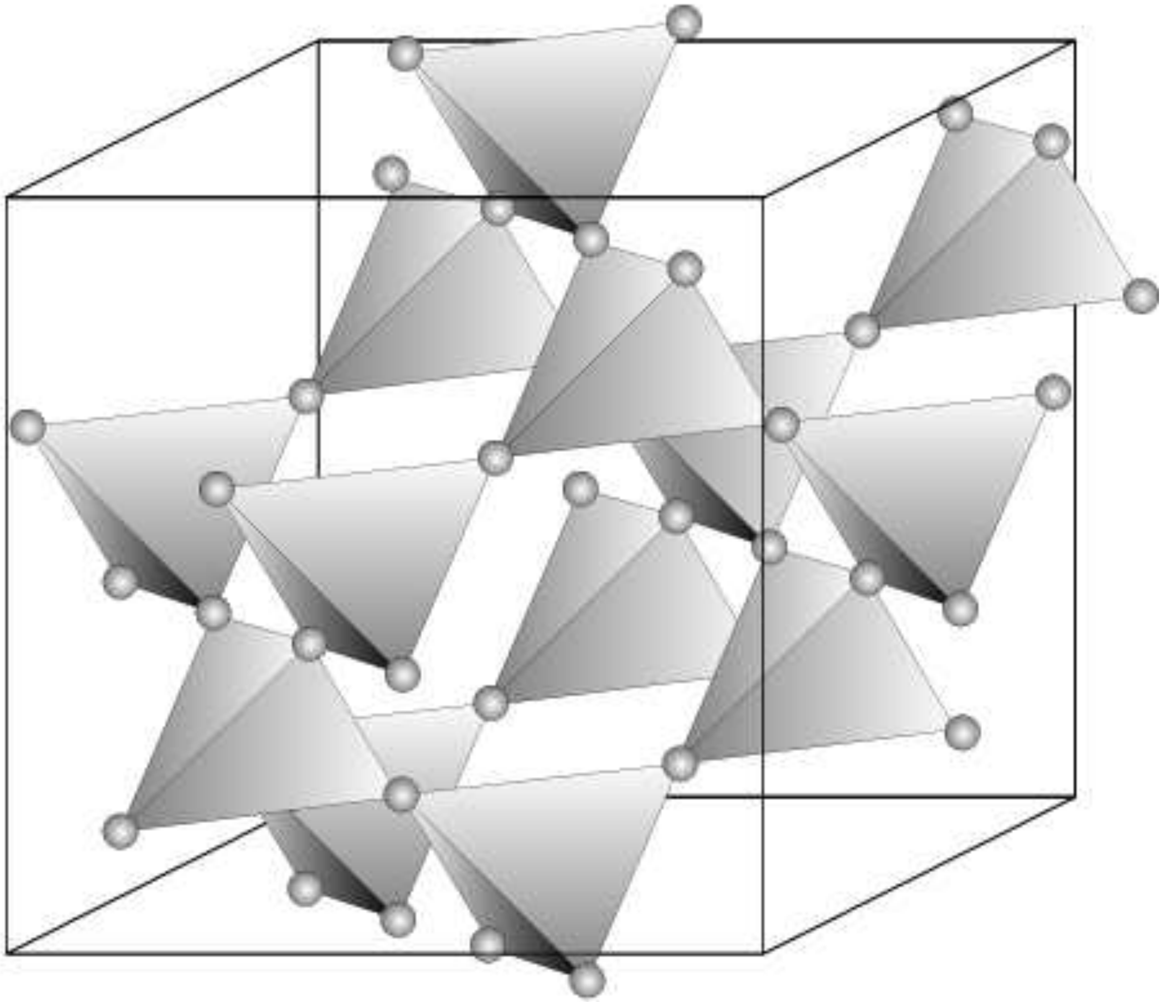

Image credit: http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_2/basics/b2_1_6.html

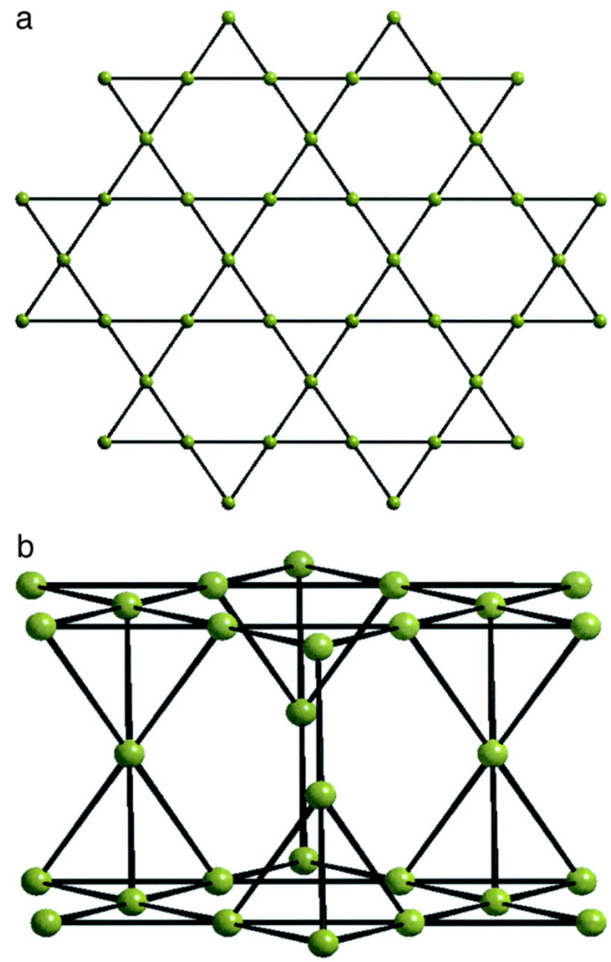
# But the B atoms form a pyrochlore lattice of corner shared tetrahedra => frustration



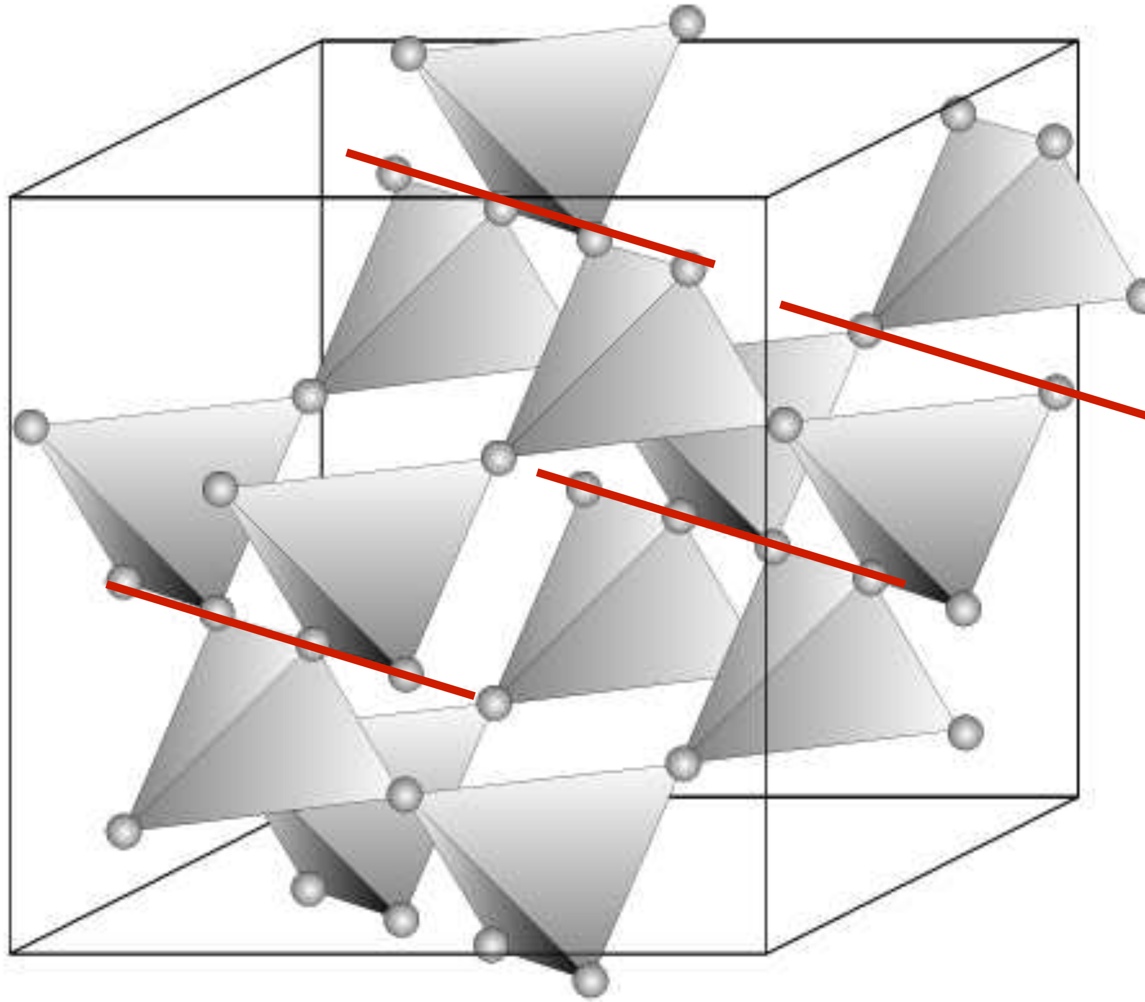


# But the B atoms form a pyrochlore lattice of corner shared tetrahedra => ~~frustration~~





# But the B atoms form a pyrochlore lattice of corner shared tetrahedra => low dimensional physics!



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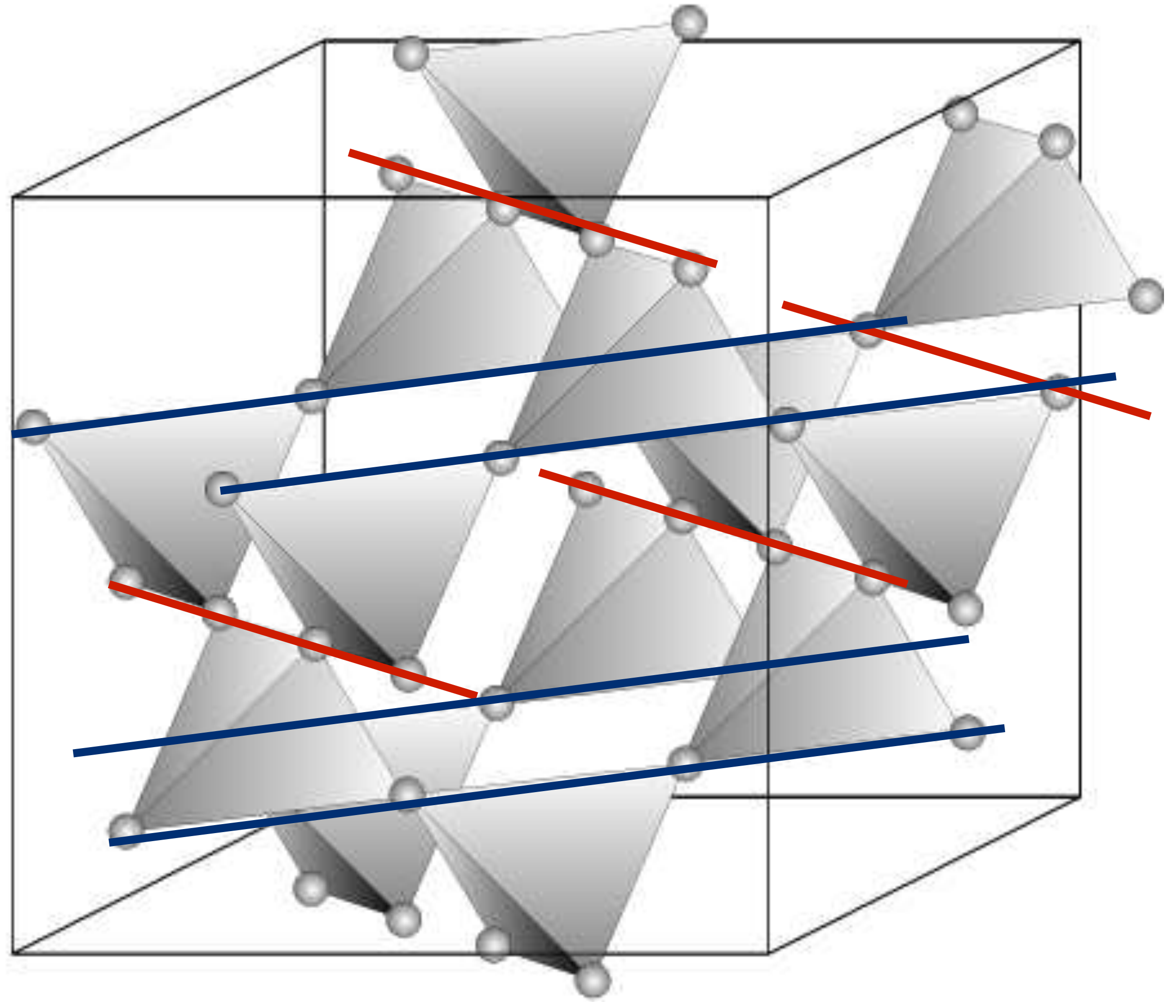

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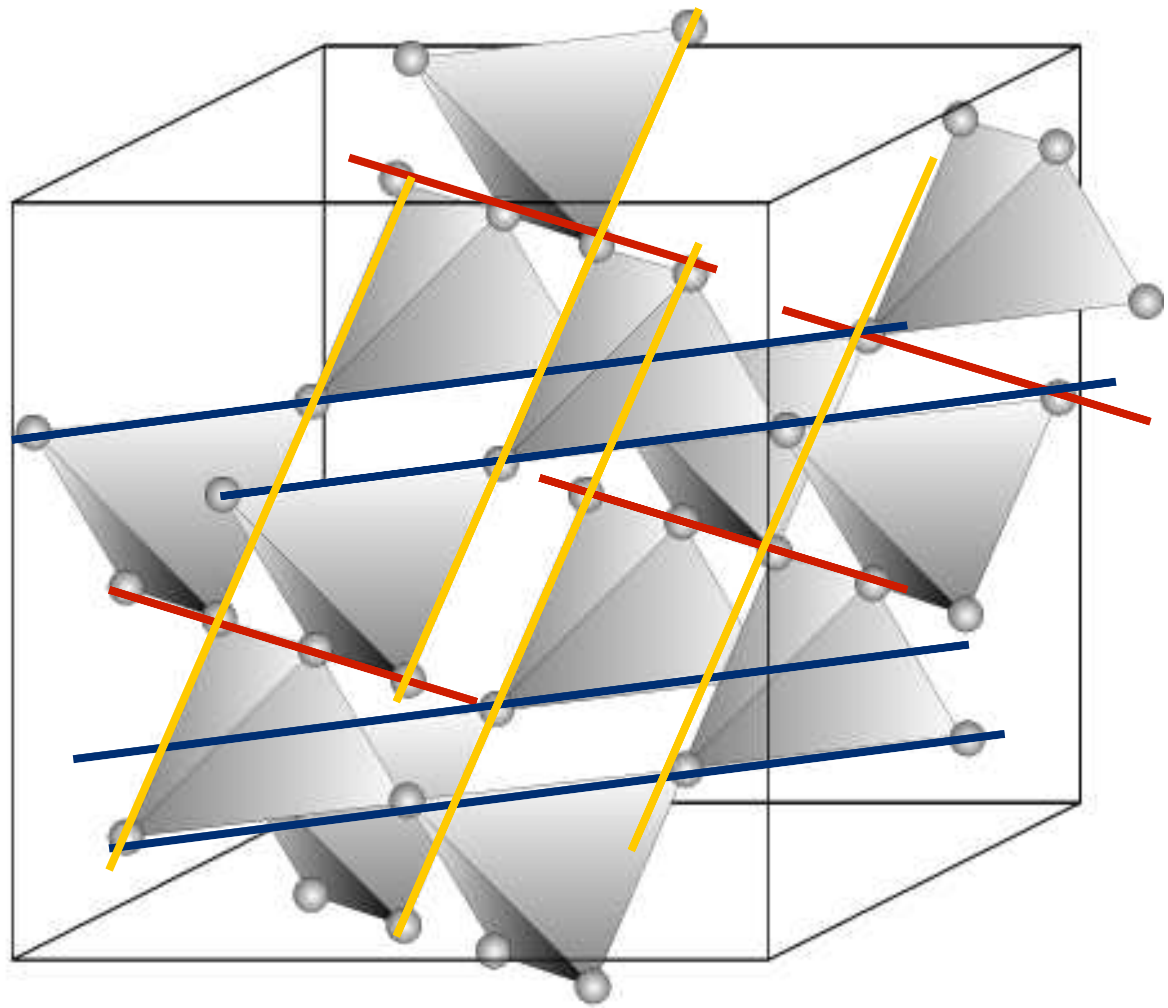
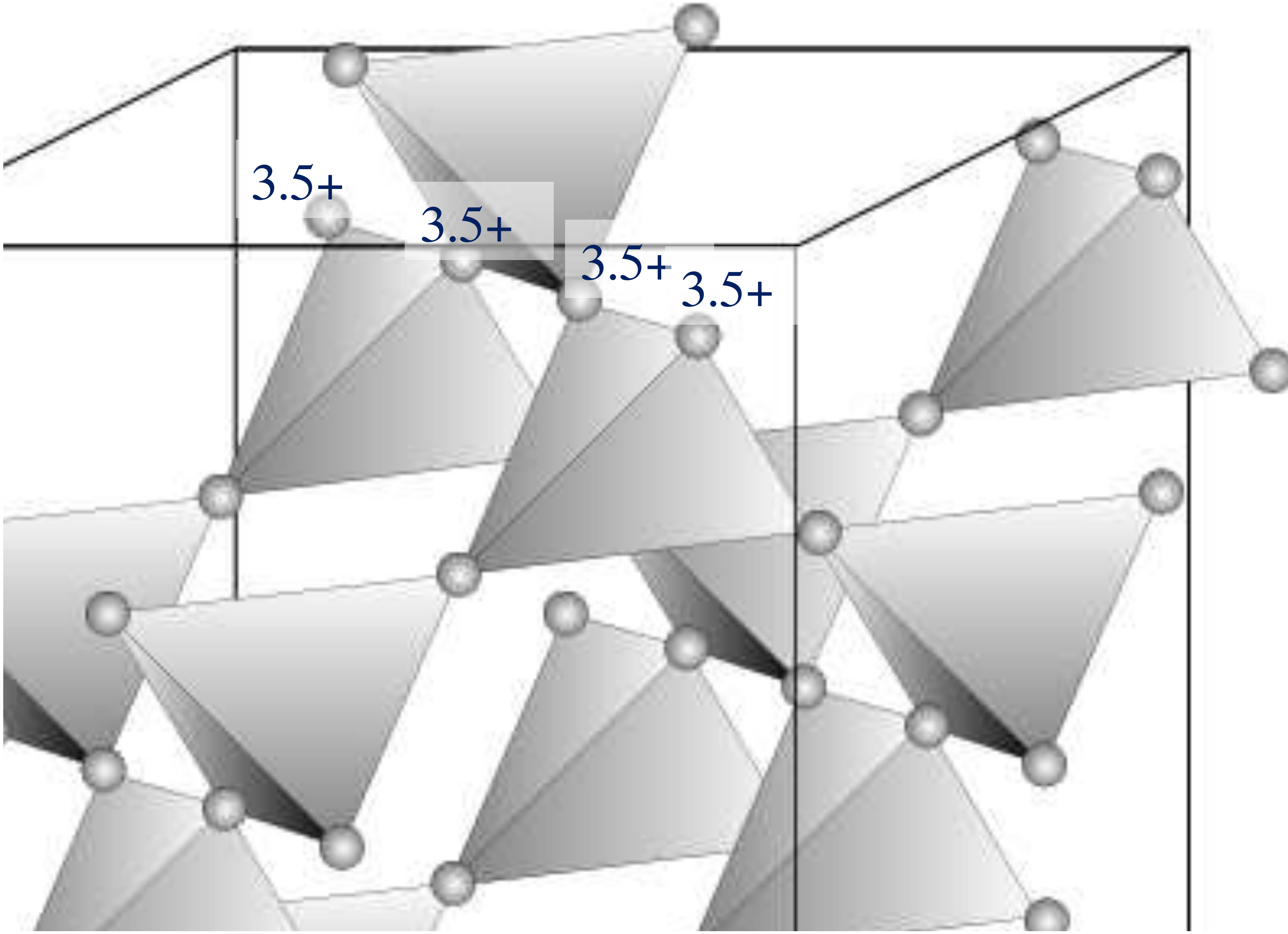
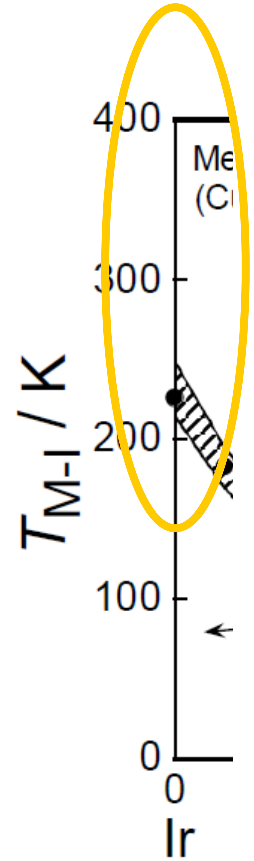
# But the B atoms form a pyrochlore lattice of corner shared tetrahedra => low dimensional physics!



# $CuIr_2S_4$




05).

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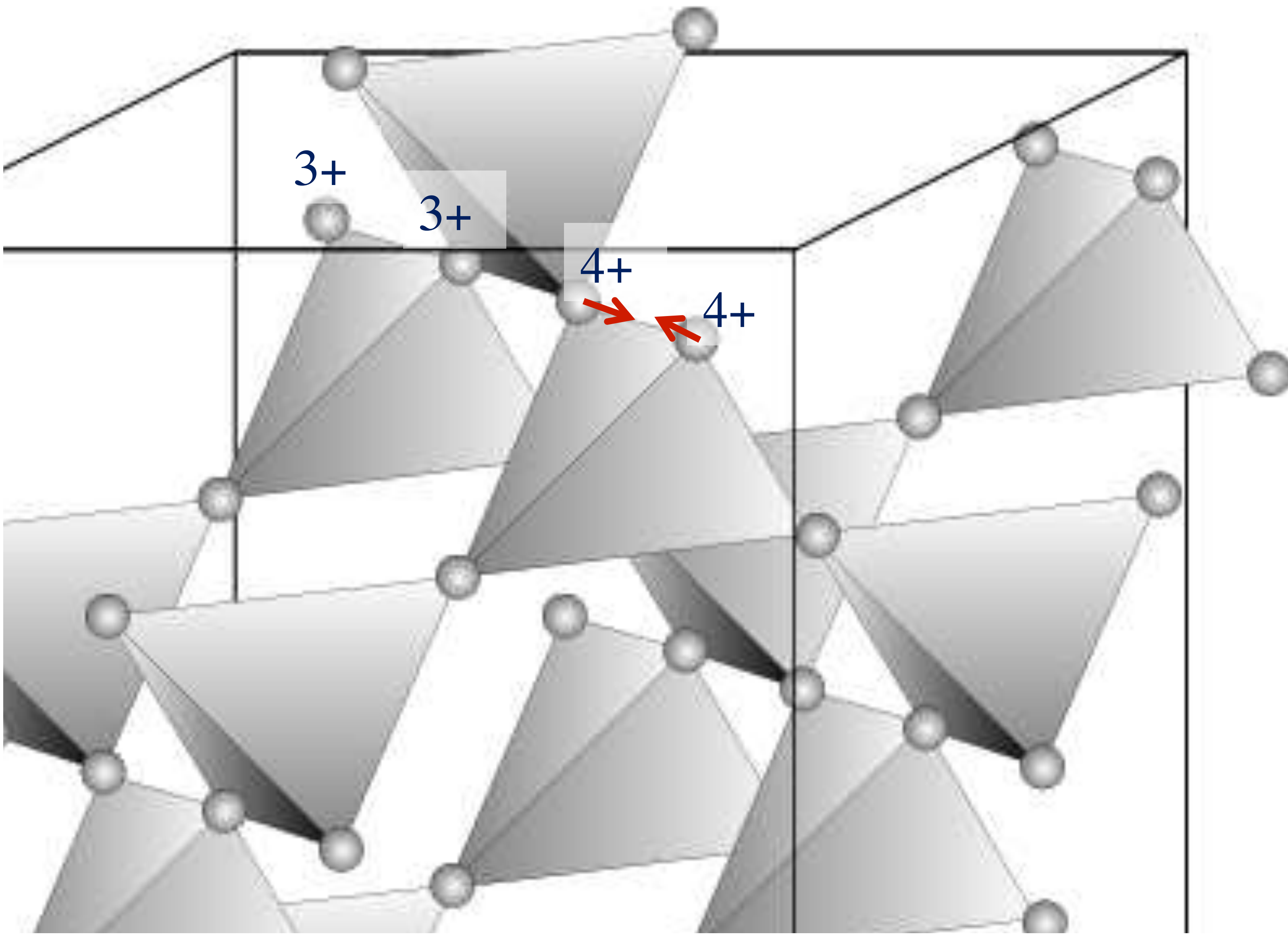
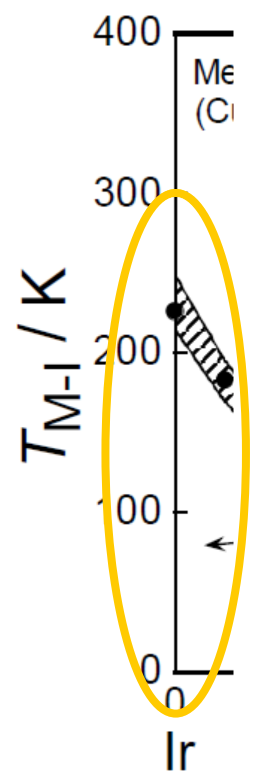
CuIr$_2$S$_4$

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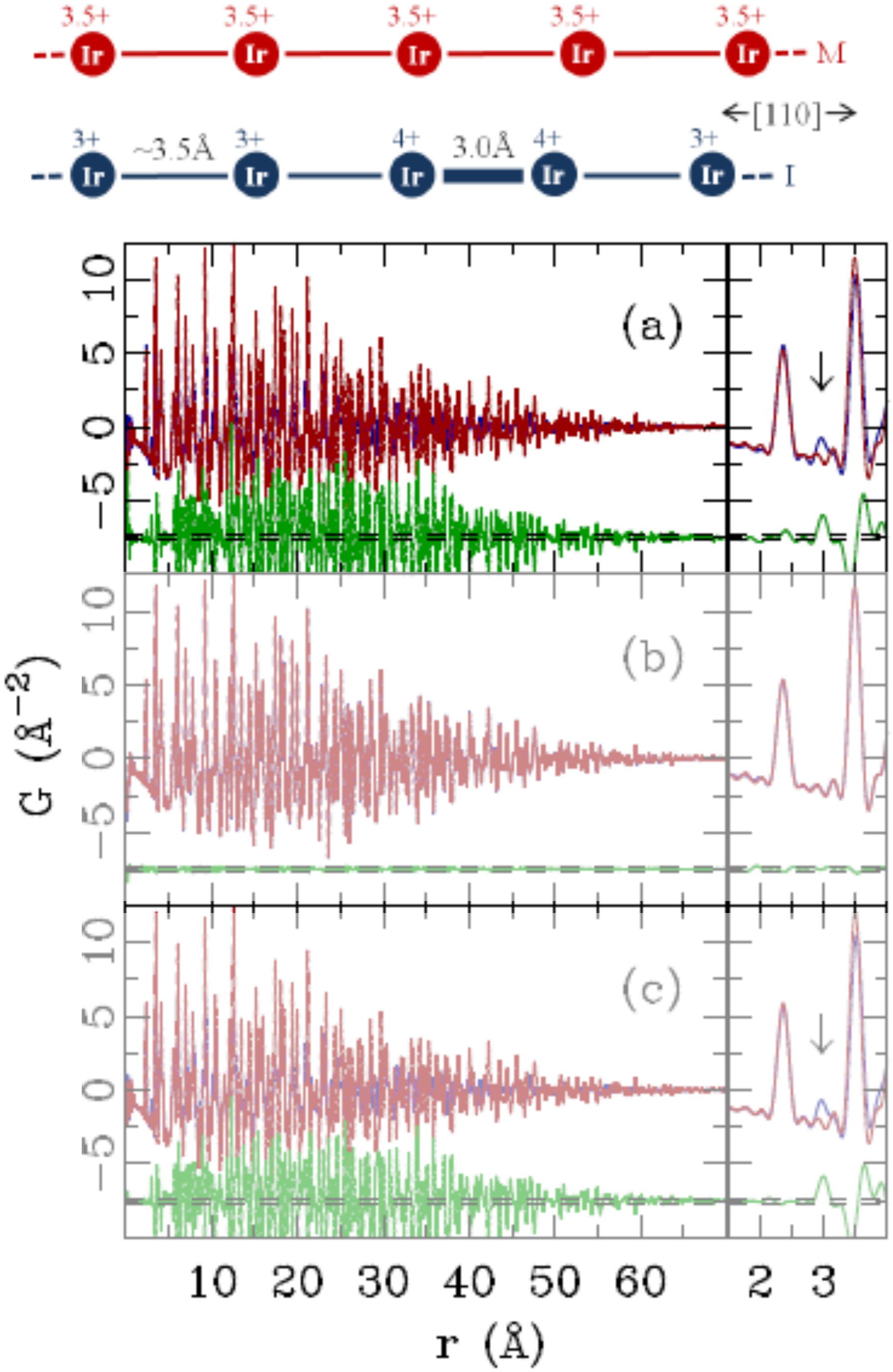
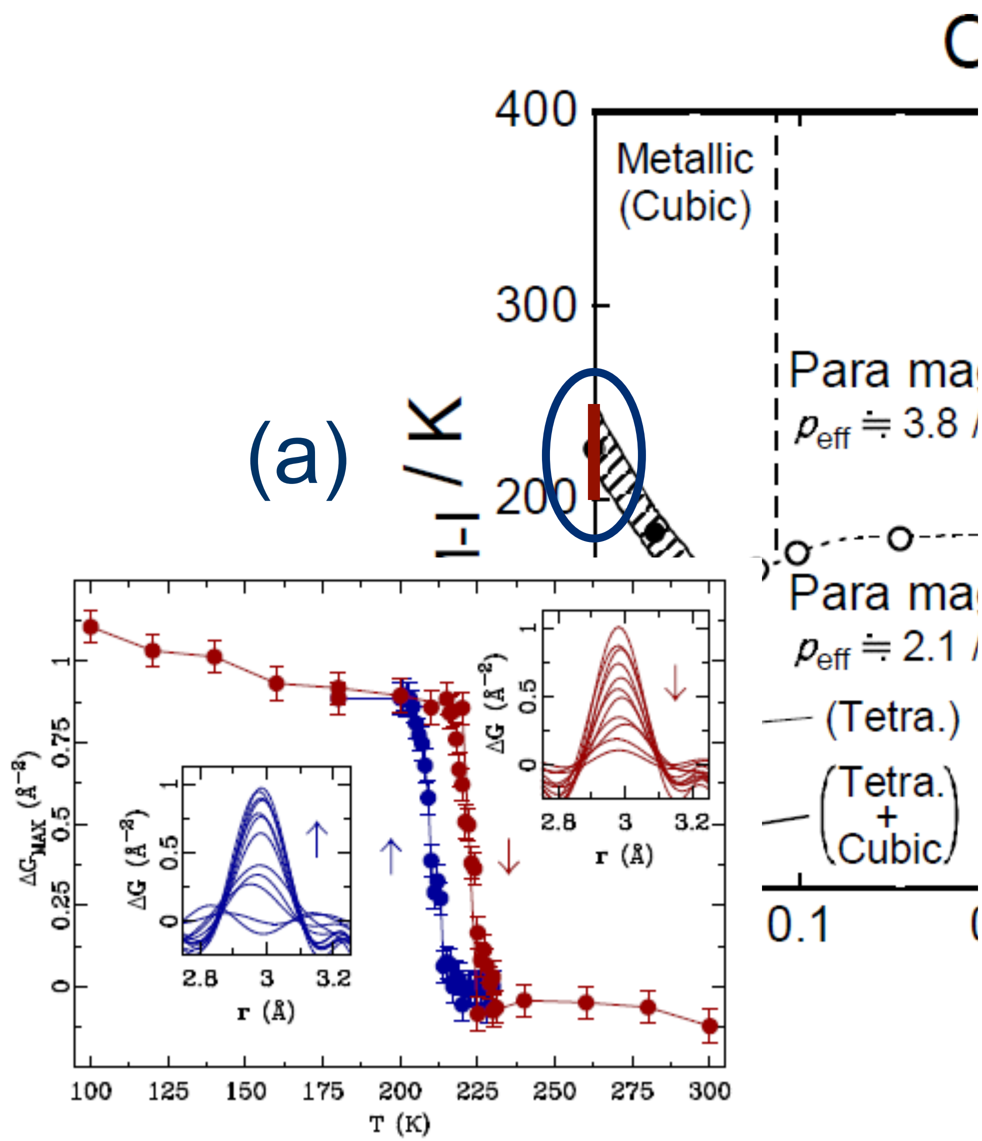
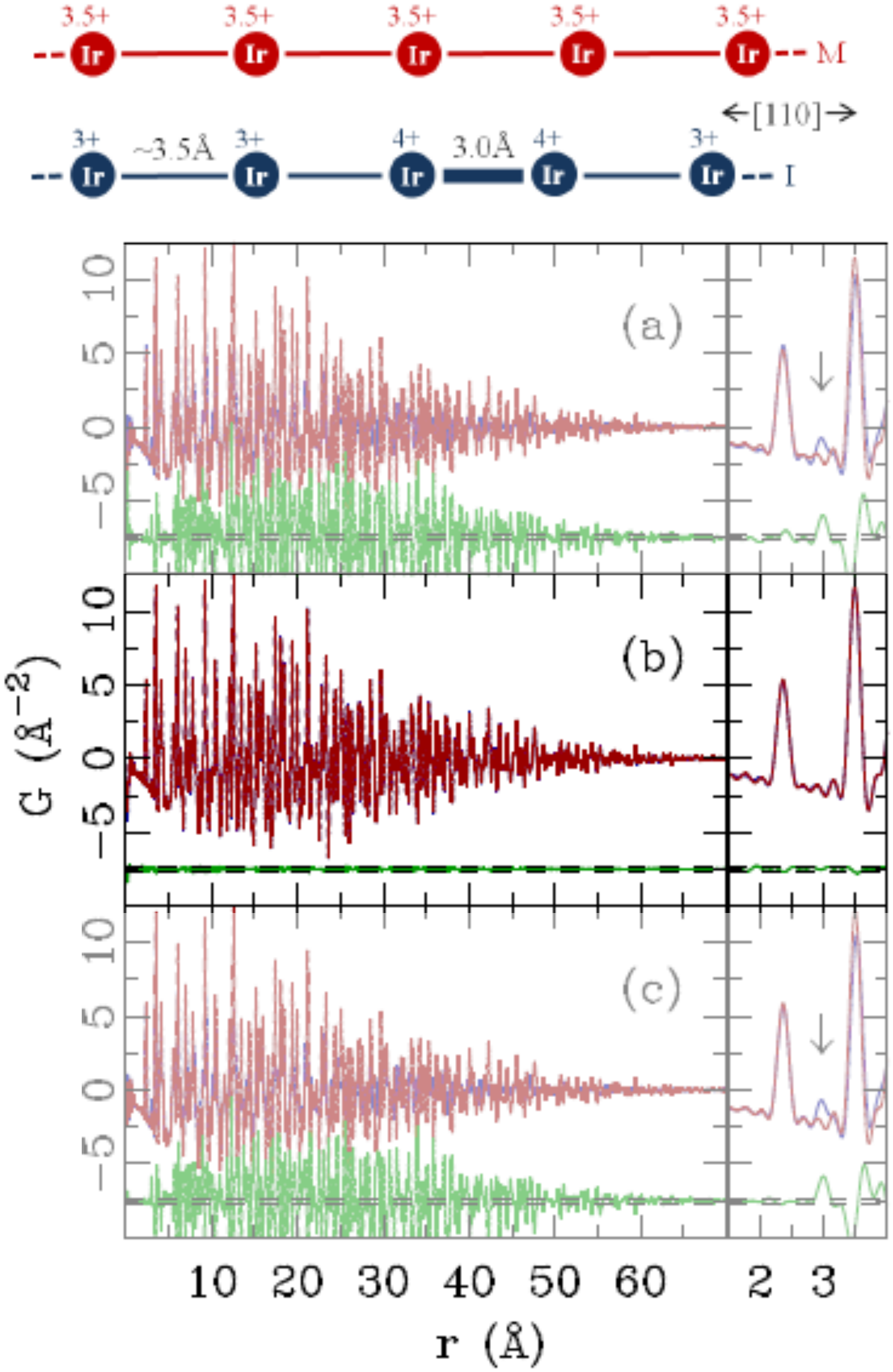
$CuIr_2S_4$

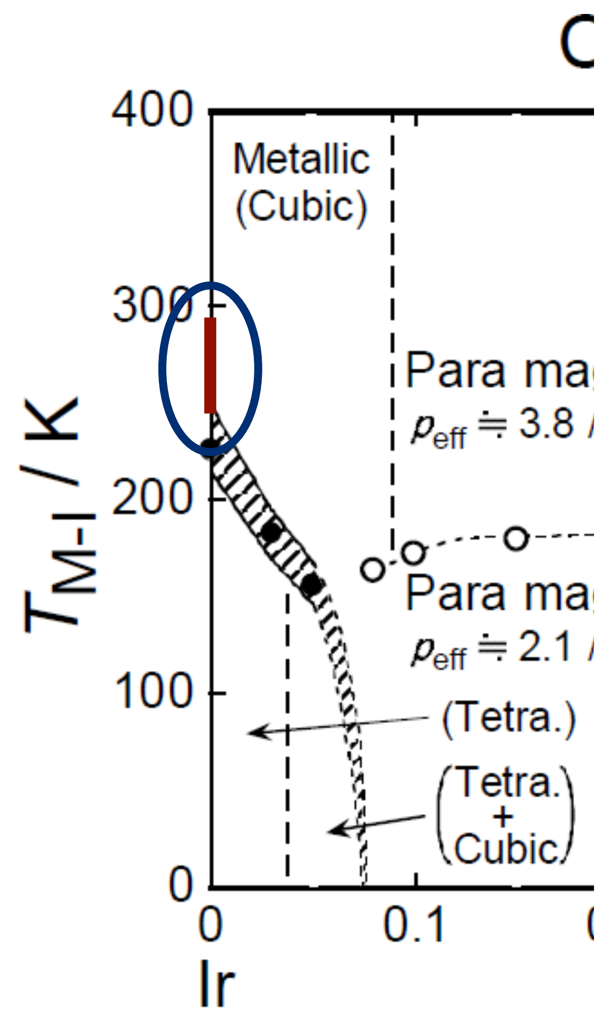

3.5+
Ir
M
←[110]→
3+
~3.5Å
4+
3.0Å
I
(a)
(b)
(c)
G (Å$^{-2}$)
r (Å)



(a)
Metallic
(Cubic)
Para ma
$p_{eff}$ ≑ 3.8
$p_{eff}$ ≑ 2.1
(Tetra.)
Tetra.
+
Cubic
0.1
$\Delta G_{MAX}$ (Å$^{-2}$)
$\Delta G$ (Å$^{-2}$)
r (Å)
T (K)




# $CuIr_2S_4$

(b)

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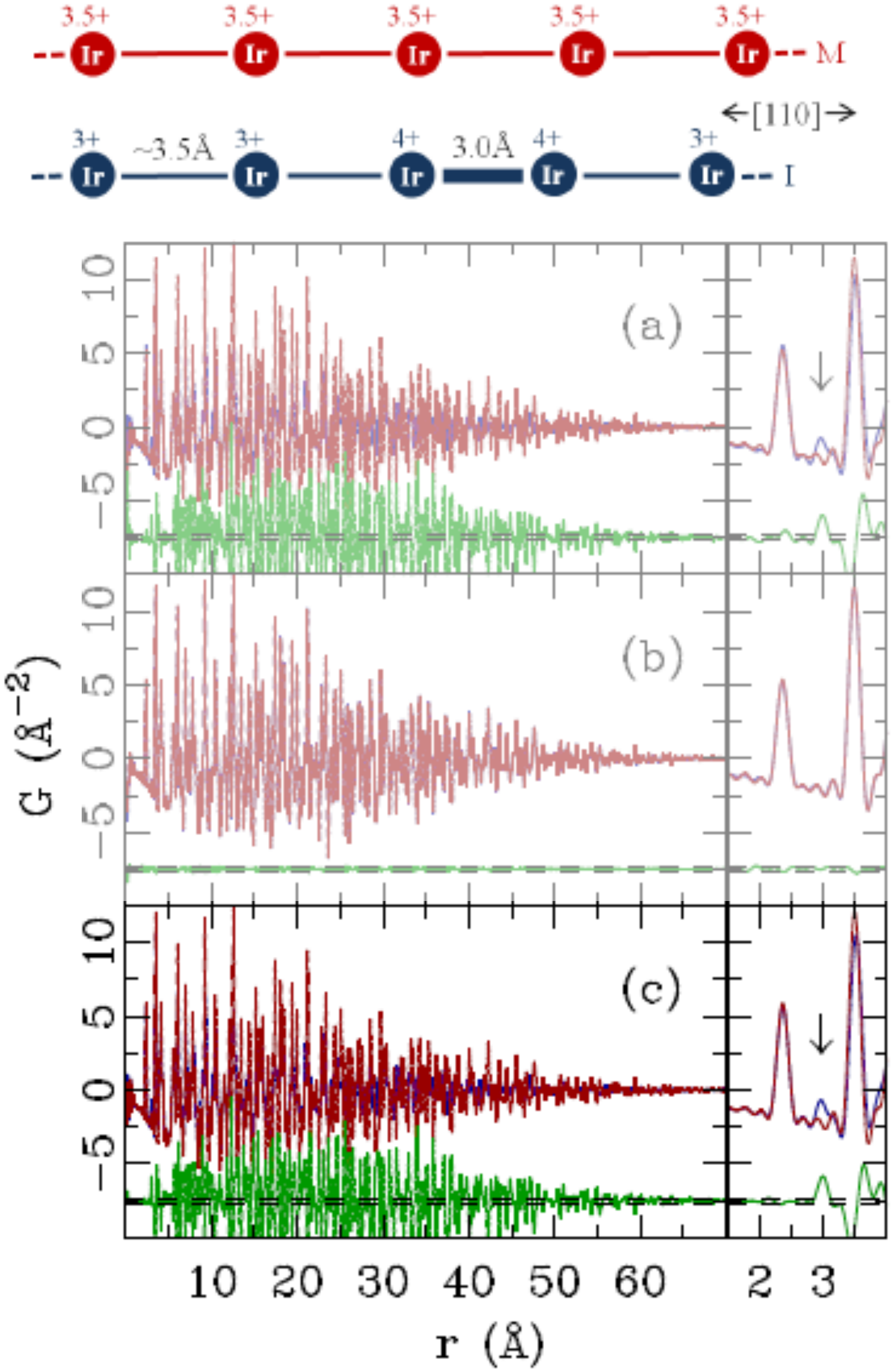
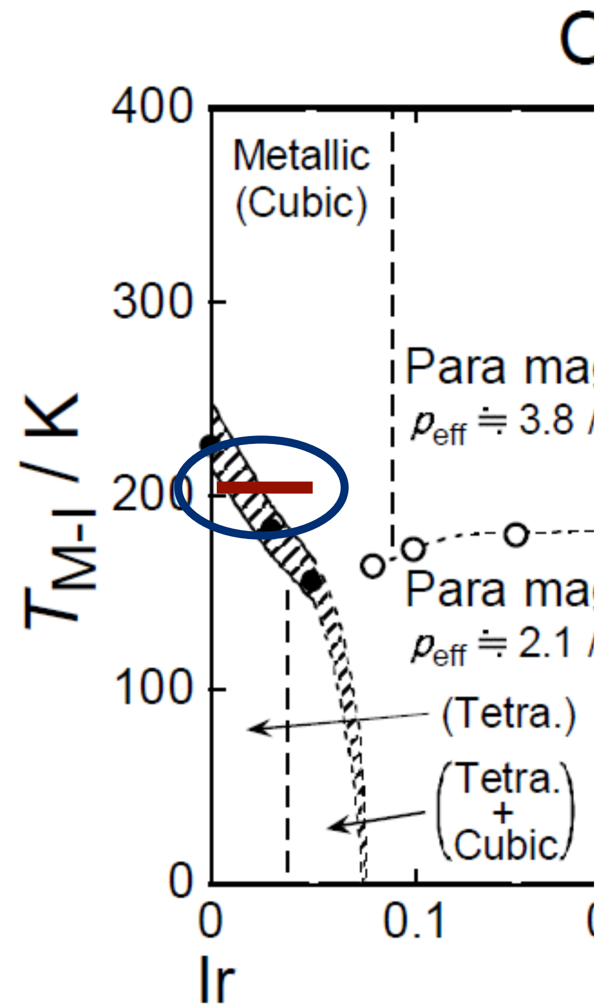



# $CuIr_2S_4$

(c)

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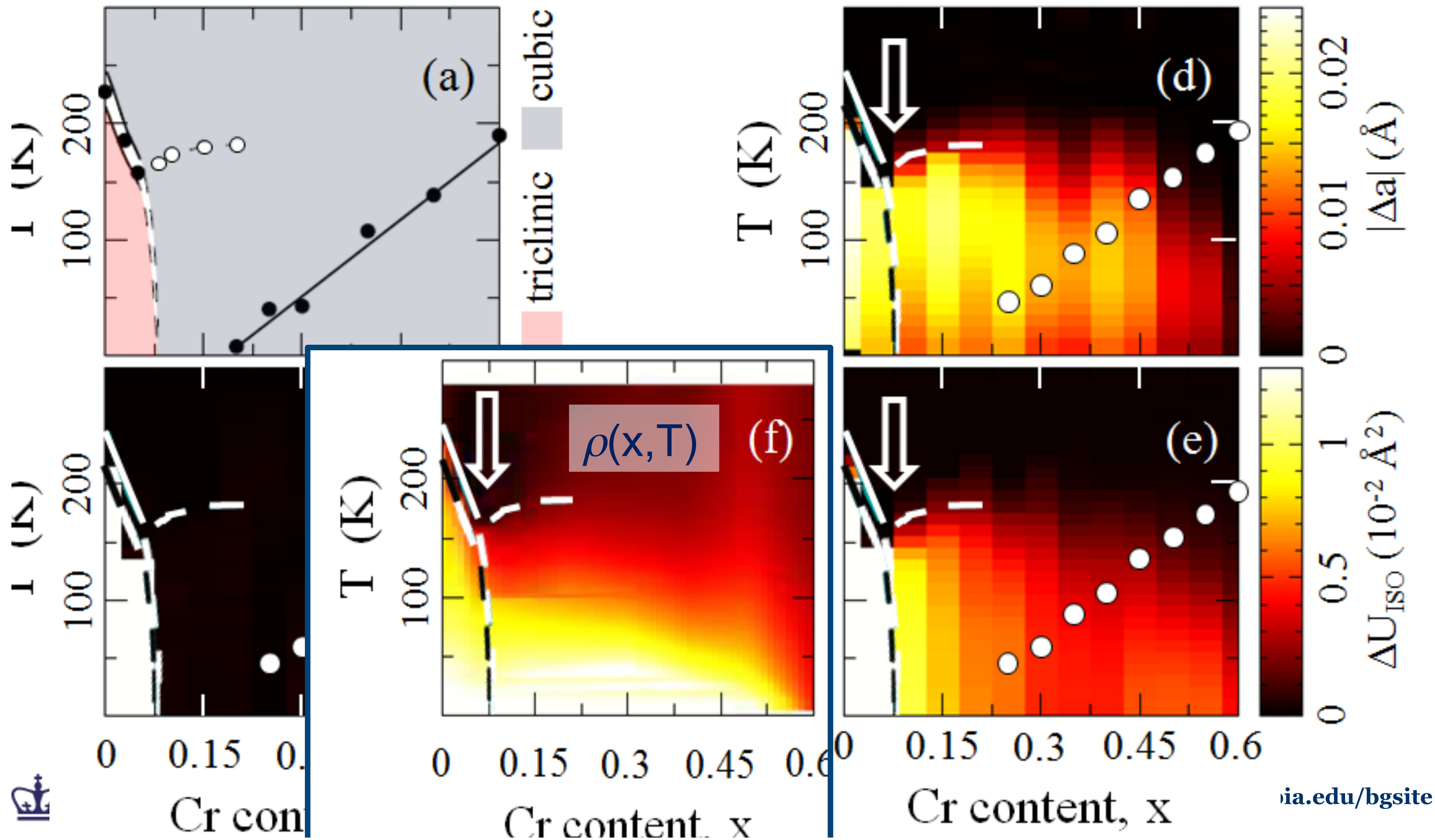
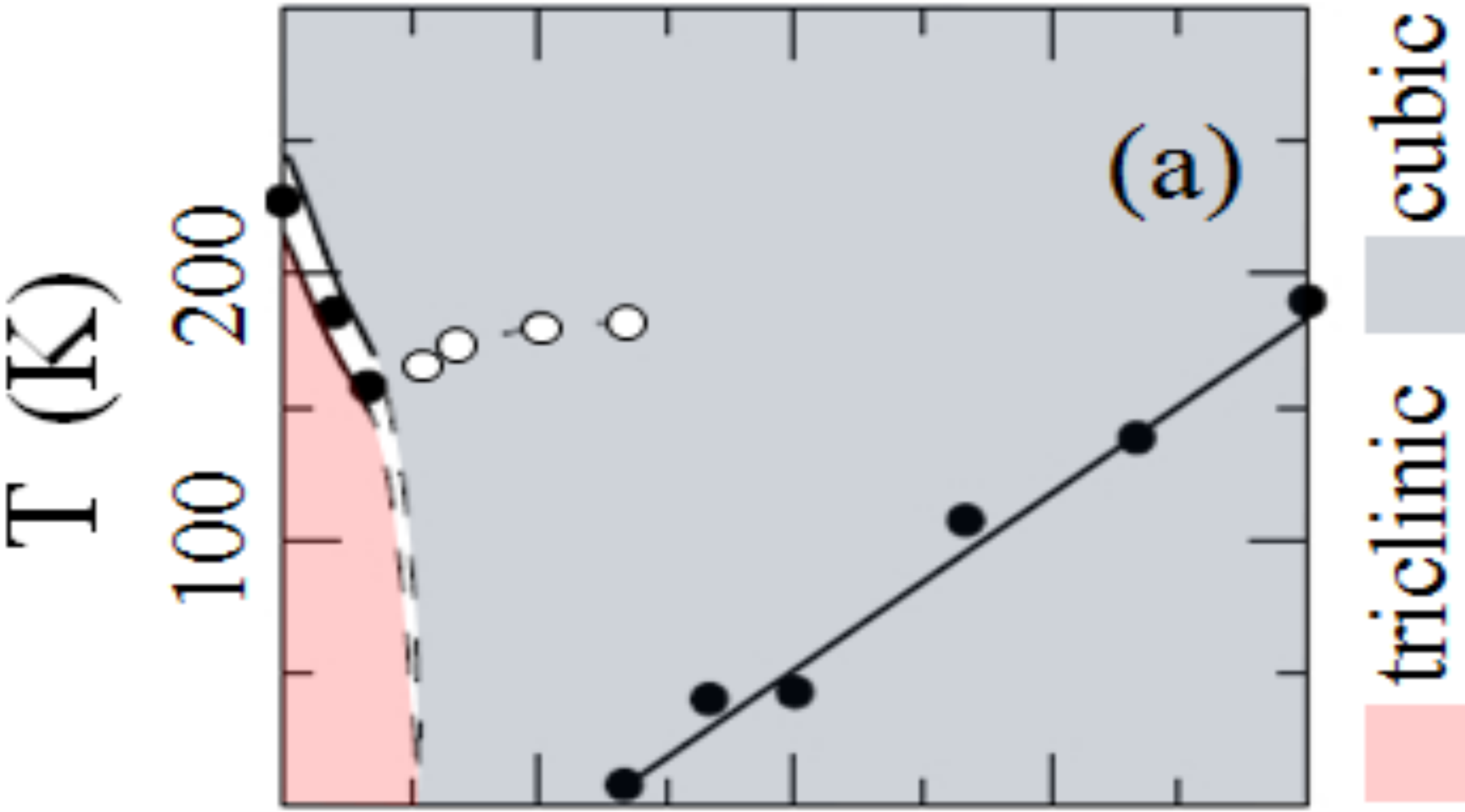
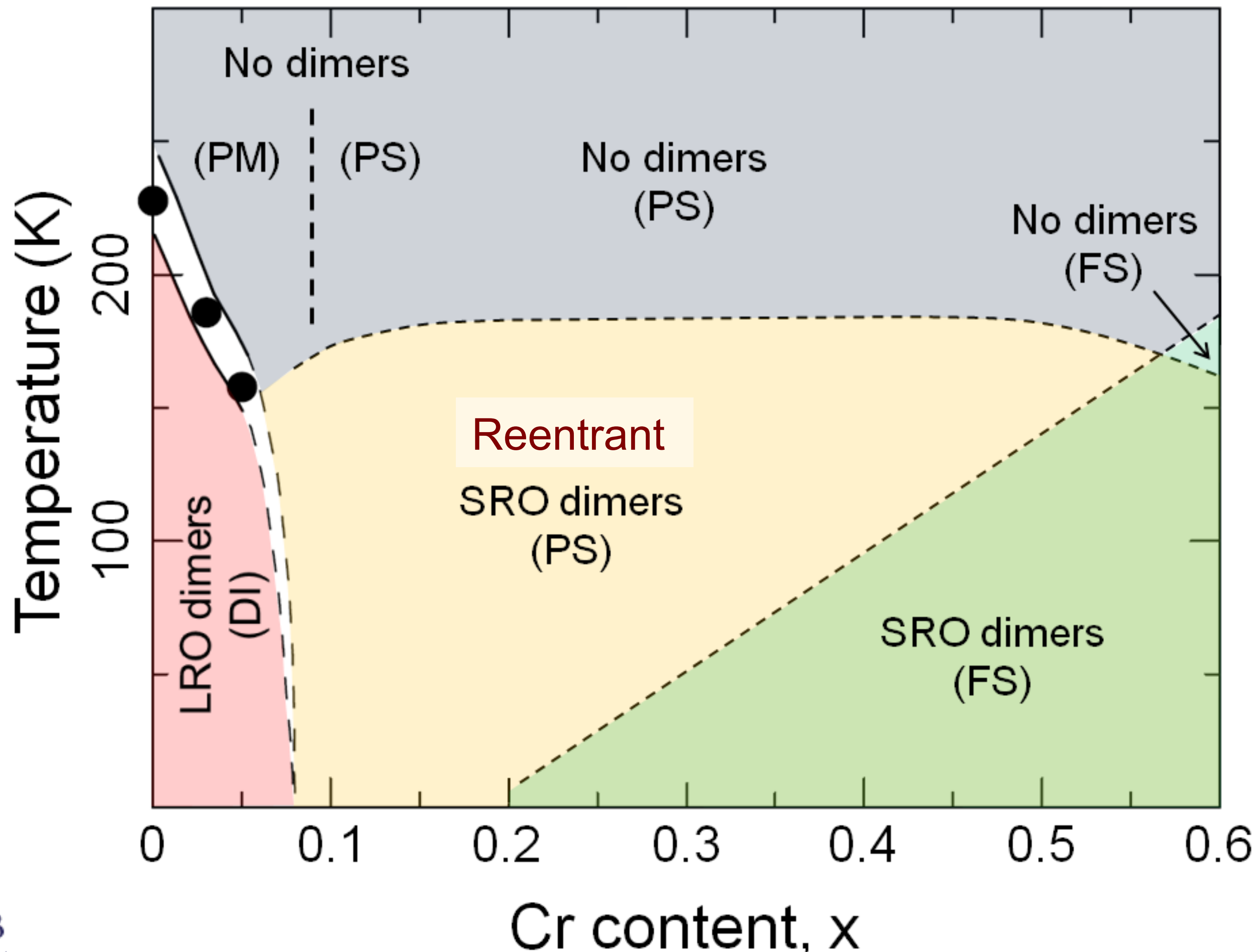


Avg str
Local str
(a)
cubic
triclinic
(d)
|Δa| (Å)
(e)
$\Delta U_{ISO}$ ($10^{-2}$ Å$^2$)
(f)
ρ(x,T)
T (K)
Cr content, x

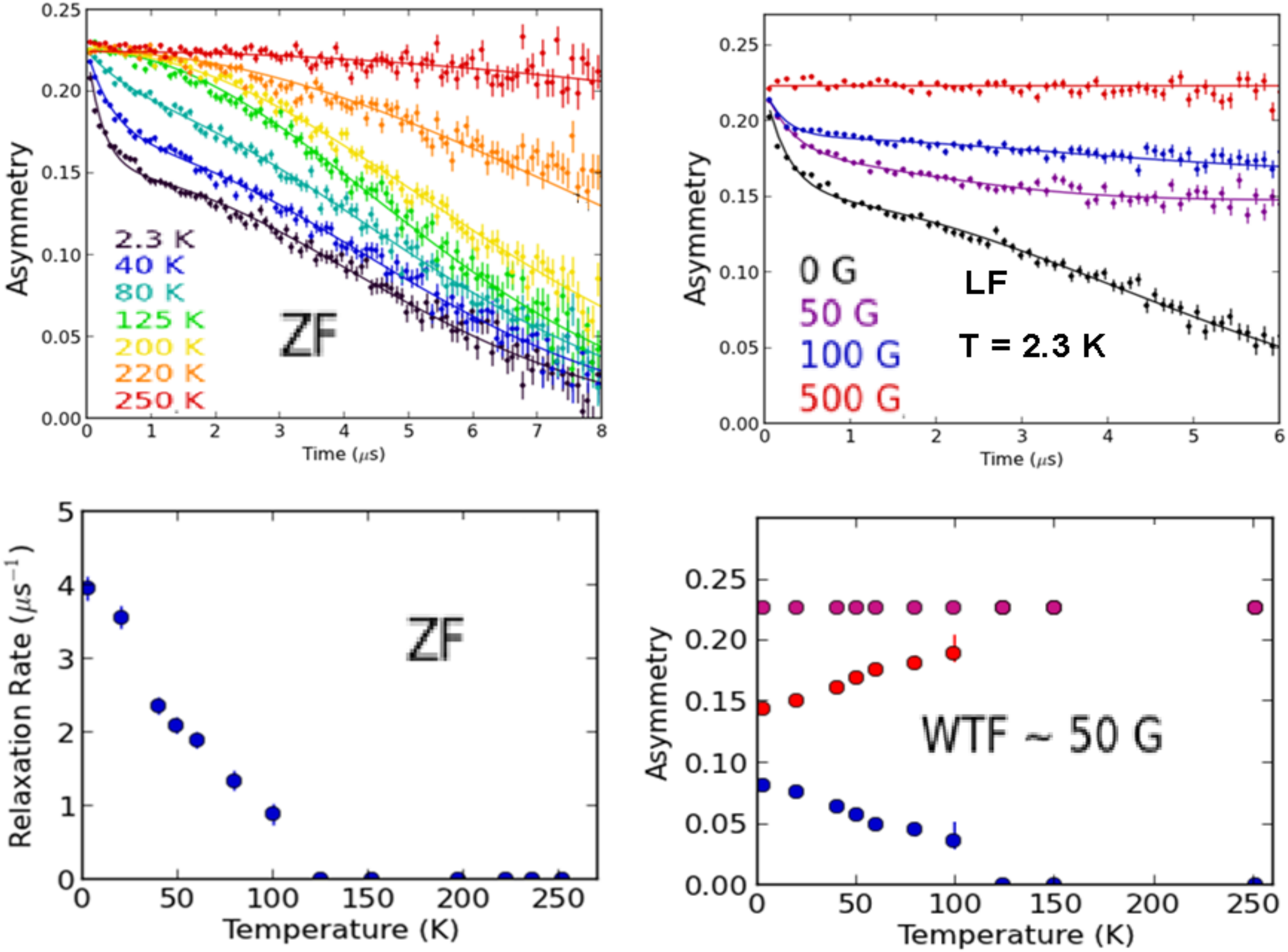
# Average phase diagram



# Local phase diagram



# Results: x = 0



Asymmetry
Time (μs)
2.3 K
40 K
80 K
125 K
200 K
220 K
250 K
ZF
0 G
50 G
100 G
500 G
LF
T = 2.3 K
Relaxation Rate ($\mu s^{-1}$)
Temperature (K)
WTF ~ 50 G

# Acknowledgements


- A special thank you to all my current and former students and post-docs
- Emil Bozin, Milinda Abeykoon, Pavol Juhas
- Also my many wonderful collaborators, in particular from the work described here: John Mitchell, John Tranquada, John Hill, Weiguo Yin, Genda Gu
- Facilities:
  - NSLS (and people therein)
  - Lujan Center LANL (and people therein)
  - Triumph, Canada
- Funding: DOE-BES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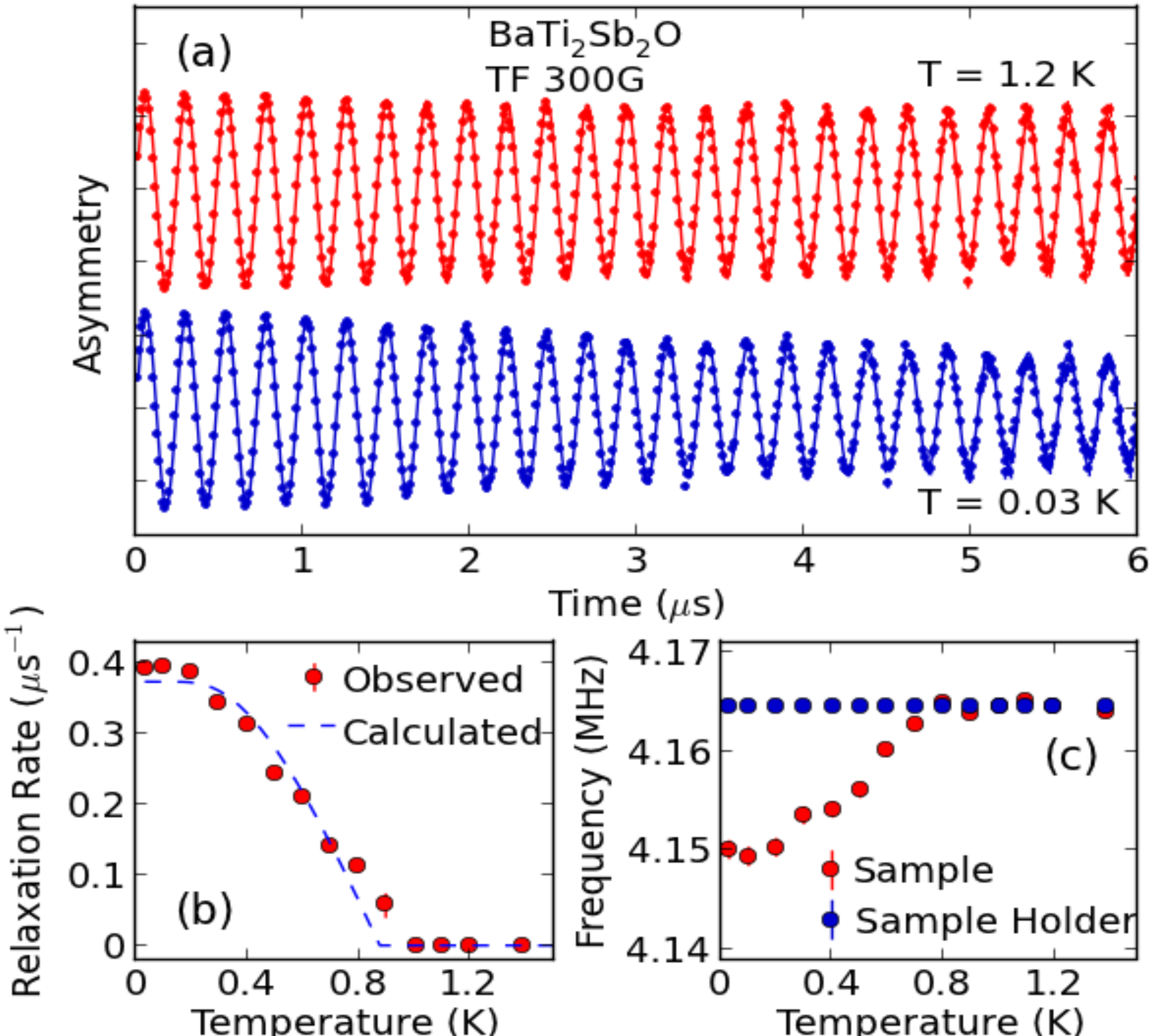
# Superconductivity probed by μSR




Conclusion: fully gapped s-wave superconductivity

Tc ≈ 1 K

$\lambda_L$ (T = 0) ≈ 430 nm

Agreement with other μSR and heat capacity studies (von Rohr et al, PRB 88: 140501 (2013); Gooch et al, PRB 88: 064510 (2013))

Y. Nozaki et al. PRB 88 214506 (2013)

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